

POLYMERISATION PROCESS

This invention relates to polymeric materials; more particularly this invention relates to polymeric materials comprising cross-linked particles which are capable of forming sols; to processes for their preparation; and to compositions comprising them.

05 According to one aspect of this invention, there is provided a solution polymerisation process for the preparation of a polymeric material having a weight average molecular weight from 5,000 to 20,000,000 and comprising cross-linked particles which are capable of forming a sol in the reaction solvent, which process comprises:

- 10 (i) polymerising one or more monomers, the or at least one of which is a cross-linking agent, in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture;
- 15 (ii) monitoring the polymerisation until a polymeric material as herein defined is obtained; and
- 20 (iii) terminating the polymerisation before gelation is obtained.

The solution polymerisation process of the invention may be an addition, for example a cationic, anionic or free radical, polymerisation or a condensation polymerisation.

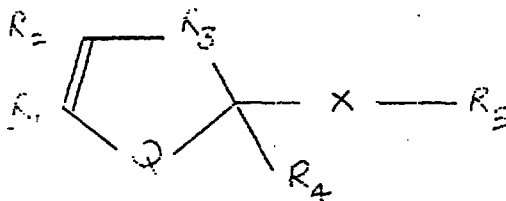
25 A class of addition polymerisation to which the present invention may advantageously be applied is cationic addition polymerisation to which the following types of monomer, inter alia, are susceptible:

- (a) cyclic and linear mono- and poly-vinyl (thio)ethers, including furfural and furfuryl alcohol;
- 30 (b) other compounds comprising at least one 3- or 4- membered oxa- or thia- substituted ring, for example mono- and poly-epoxides and lactones with a 4-membered ring;
- (c) cyclic aliphatic anhydrides, for example maleic anhydrides;
- (d) aliphatic aldehydes; and

(e) mono- and poly-vinyl aromatic hydrocarbons, such as styrene, alkyl styrenes, such as vinyl toluene, divinyl benzene and indene.

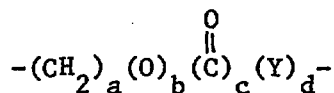
Mixtures of such monomers may be used.

- 05 In accordance with a preferred aspect of this invention the, or one of the, monomers comprises a polymerisable cyclic (thio)ether. By "(thio)ether" is meant herein an ether or a thioether. Suitable polymerisable cyclic (thio)ethers have the formula:



in which:

- 10  $R_1$ ,  $R_2$  and  $R_4$ , which may be the same or different, each represent a hydrogen atom or a substituted or unsubstituted hydrocarbyl or hydrocarbyloxy group;
- $R_3$  represents a substituted or unsubstituted methylene, ethylene or 1,3-propylene group;
- 15  $R_5$  represents a monovalent polymerisable group;
- $Q$  represents an oxygen or a sulphur atom; and
- $X$  represents:



in which:

- $Y$  represents an oxygen atom or a  $-NR_6$ -group wherein  $R_6$
- 20 represents any of the values which  $R_1$  may assume;
- $a$  is 0 or 1;
- $b$  is 0 or 1;
- $c$  is 1 or 2;
- $d$  is 0 or 1;

- 25 with the proviso that at least one of  $b$  or  $d$  is 1.

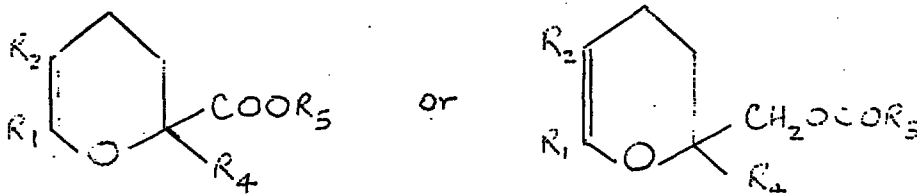
The groups  $R_1$ ,  $R_2$  and  $R_4$  may each represent a substituted or unsubstituted hydrocarbyl or hydrocarbyloxy group: examples include unsubstituted or halo-substituted  $C_1$  to  $C_4$  alkyl, such as

05 methyl or ethyl; unsubstituted or halo-substituted  $C_6$  to  $C_{10}$  aryl or aralkyl, such as phenyl or benzyl; and oxy analogues. In the case of  $R_4$ , increase in the size of the group increases the steric hindrance to the hydrolysable ester or amide function X and thereby increases the stability of the polymer. It is preferred, however, from the standpoint of ease of preparation and availability, that at least one, and preferably all, of  $R_1$ ,  $R_2$  and  $R_4$  represents a hydrogen atom. The group  $R_3$  may represent a mono- or poly- substituted ethylene group, preferably an unsubstituted ethylene group; that is, a dihydro(thia)pyran derivative.

10 Preferred such compounds are ethers; that is, those compounds of the above formula wherein Q represents an oxygen atom, especially dihydropyrans.

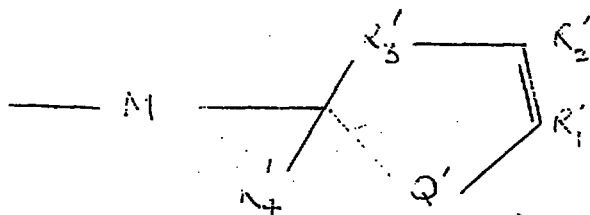
15 X may, as shown, represent any hydrolysable carboxylic acid ester, carbonate ester or oxalate ester function, or an amide analogue. Preferably, however, X represents  $-COO-$  or  $-CH_2OCO-$ .

Particularly preferred polymerisable cyclic ethers have the formula:



20  $R_5$  may suitably represent any group which can participate in cationic polymerisation; for example those derivable from monomers (a) to (e) mentioned hereinbefore. Preferred examples are vinyl (thio)ether and epoxy groups.

It is particularly preferred that  $R_5$  represents a cyclic vinyl (thio)ether, especially of the formula:



in which:

$R_1'$ ,  $R_2'$ ,  $R_3'$  and  $R_4'$ , which may be the same or different, represent any of the values which  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may assume;

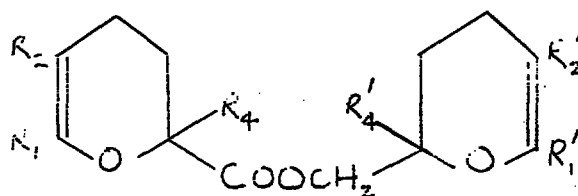
M represents the group  $-ZX'-$ ;

05  $Q'$  represents an oxygen or sulphur atom;

$X'$  represents any of the values which X may assume; and

Z represents a single bond or a substituted or unsubstituted hydrocarbylene.

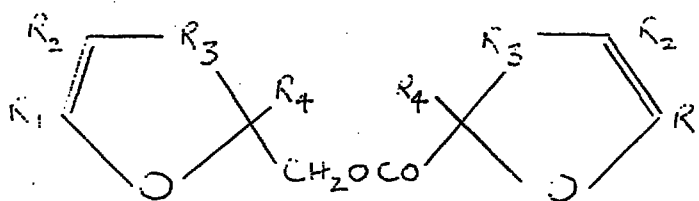
10 Especially preferred polymerisable cyclic ethers are the reaction products formed by subjecting one or a mixture of dihydropyran aldehydes to disproportionation by the Tischenko reaction; they have the formula:



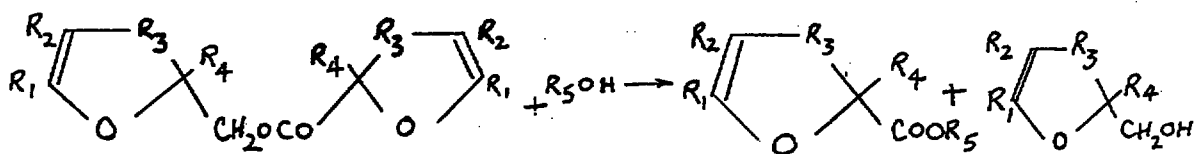
in which:

15  $R_1'$ ,  $R_2'$  and  $R_4'$ , which may be the same or different, represent any of the values which  $R_1$ ,  $R_2$  and  $R_4$  respectively may assume. A preferred such compound is acrolein tetramer (in which the  $R_1$  all represent hydrogen atoms).

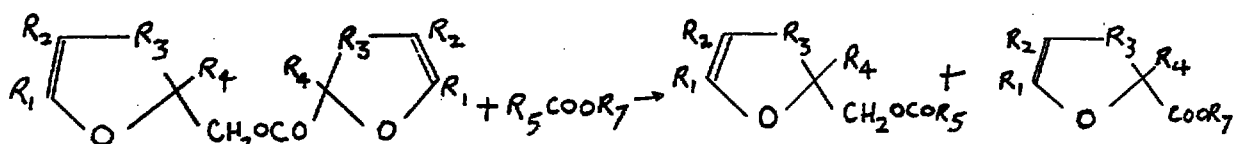
20 Polymerisable cyclic ethers wherein X comprises a  $-COO-$  or  $-CH_2OCO-$  group may conveniently be prepared from the tetramer of the corresponding unsaturated aldehyde produced by the Tischenko reaction; namely:



Thus, cyclic ethers wherein X comprises a  $-\text{COO}-$  group may be prepared by reaction of the tetramer with an alcohol  $\text{R}_5\text{OH}$  using a transesterification catalyst and reaction conditions:



05 Cyclic ethers wherein X comprises a  $-\text{CH}_2\text{OCO}-$  group may be prepared by reaction of the tetramer with a lower alkyl carboxylic acid ester  $\text{R}_5\text{COOR}_7$  in which  $\text{R}_7$  represents a lower alkyl group using a transesterification catalyst and reaction conditions:



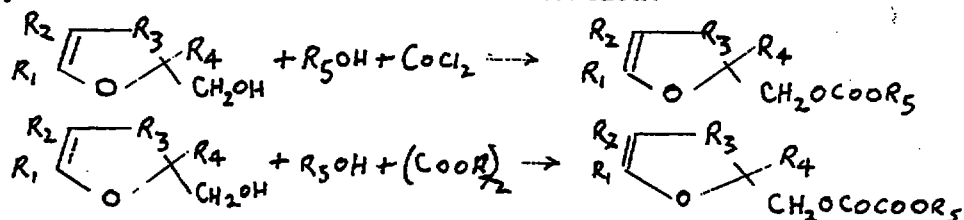
The respective by-products may also be transesterified with  $\text{R}_5\text{COOR}_7$  or  $\text{R}_5\text{OH}$  to give, correspondingly:



10 The corresponding amides may be prepared analogously.

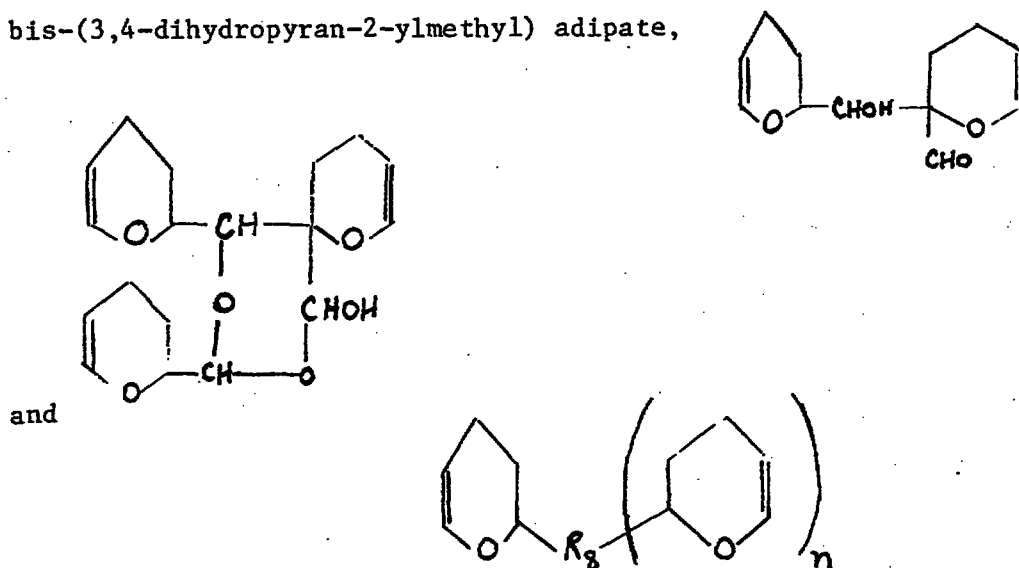
Cyclic ethers where X comprises a  $-\text{COO}-$  group may also be obtained by mild oxidation of the dimer of the corresponding unsaturated aldehyde, followed by esterification of the salt, for example the silver salt.

15 Meta-carbonates and oxalates may be obtained, respectively, by esterification and transesterification:



It is, however, to be stressed that acrolein tetramer is readily prepared from acrolein which is a commercially available material; can readily be purified; and has been found to be satisfactory in the practice of this invention.

05 Other specific examples of polymerisable cyclic ethers include bis-(3,4-dihydropyran-2-ylmethyl) succinate, bis-(3,4-dihydropyran-2-ylmethyl) o-terephthalate, bis-(3,4-dihydropyran-2-yl) adipate, bis-(3,4-dihydropyran-2-ylmethyl) adipate,



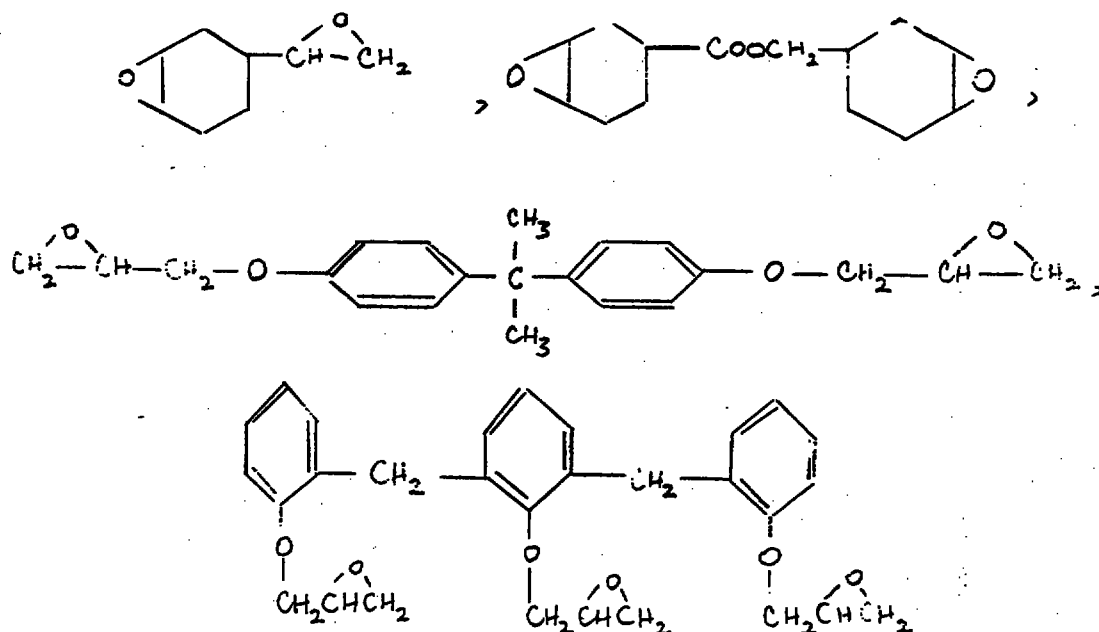
10 wherein:

n represents a number of at least one; and R<sub>g</sub> is a polyvalent organic bridging group which desirably does not contain a basic group since these can interfere with the acid catalysis required, as will be explained later, for the polymerisation.

15 A further class of addition polymerisation to which the present invention may also advantageously be applied is free radical addition polymerisation. Suitably the, or one of the, monomers comprises a vinyl- or vinylidene group-containing monomer, preferably a substituted or unsubstituted (meth)acrylate ester, especially a C<sub>1</sub> to C<sub>8</sub> alkyl methacrylate. Specific examples of  
20 such monomers include methylacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate,

propyl methacrylate, butyl methacrylate, n-hexyl methacrylate, ethyl hexyl methacrylate, lauryl methacrylate, phenyl acrylate, isodecyl methacrylate, 2-ethoxyethyl methacrylate, 2-n-butoxy ethyl methacrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, 2-phenoxyethyl acrylate and 2-phenoxyethyl methacrylate. Such monomers require the presence of a bis- or tris-vinyl or vinylidene group-containing monomer as cross-linking agent. This may be a hydrocarbon, for example an unsubstituted or hydrocarbyloxyated aromatic hydrocarbon such as divinyl benzene. Preferably, however, the cross-linking agent comprises a bis- or tris- vinyl or vinylidene group-containing ester, particularly preferred examples being the bis-methacrylate ester of polyethylene glycol, the bis-methacrylate ester of ethylene glycol or triallyl cyanurate.

Cationically polymerisable monomers in classes (b) and (e) above may also be free radical polymerised. Of these, epoxides and episulphides are particularly versatile, being also susceptible to anionic addition polymerisation, for example with organometallic initiators. Suitable monoepoxides include the alkylene oxides such as ethylene oxide, propylene oxide and butylene oxides; the aromatic oxides such as styrene oxide. Polyepoxides include many commercially available (cyclo)aliphatic and aromatic polyepoxides, such as:



Analogous mono- and polyepisulphides may also be used, especially ethylene and propylene sulphides.

There are many classes of condensation polymerisation to which the present invention is applicable; for example, condensation polymerisations for the production of polyamides, polyesters, 05 polycarbonates, phenol-formaldehydes, urea-formaldehydes, urea-melamines and polyurethanes, particularly the latter. In the preparation of polyurethanes according to the invention one of the monomers comprises a polyisocyanate, for example a diisocyanate 10 such as a (cyclo)aliphatic, araliphatic or aromatic diisocyanate. Specific examples include 2,4, and 2,6 toluene diisocyanate; (cyclo)aliphatic diisocyanates such as 1,6-hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexyl methane diisocyanate, and cyclohexylene 1,2- and 1,4- diisocyanate; and araliphatic 15 diisocyanates such as 4,4'-diphenylmethane diisocyanate.

A versatile group of cross-linking agents, particularly for polyurethanes and also for cationically polymerisable species, such as the cyclic (thio)ethers, are monomers comprising at least three groups containing a reactive hydrogen atom such as a hydroxy, 20 carboxy, amino or mercapto group (amino not being preferred for cationic polymerisation), for example those comprising at least three groups which are hydroxyl, and/or carboxyl groups.

Examples include polycarboxylic acids, polyhydric phenols, hydroxy acids and polyhydric alcohols, desirably those with less 25 than 18, preferably less than 10, carbon atoms; for example aliphatic polyols such as glycerol, erythritol, pentaerythritol, sorbitol, dulcitol, inositol, 2-ethyl-2-hydroxy-methylpropane-1,3-diol and 1,2,6-hexanetriol; aromatic polyols such as 1,2,3-trihydroxybenzene, 1,2,4-trihydroxybenzene, 1,3,5-trihydroxybenzene; 30 araliphatic polyols; hydroxy aliphatic, alicyclic and aromatic carboxylic acids, including Krebs cycle acids, such as citric acid, malic acid, tartaric acid, 2-hydroxy-3-methyl (D) succinic acid, ascorbic acid, 2,3,-dihydroxybenzoic acid, 2,4,-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 35 2,3,4-trihydroxybenzoic acid, 2,4,5-trihydroxybenzoic acid, 2,4,6-trihydroxybenzoic acid and 3,4,5-trihydroxybenzoic acid. Mixtures

of polycarboxylic acids, polyhydric phenols, hydroxy acids and polyhydric alcohols may be used. Preferably the polycarboxylic acids, polyhydric phenols, hydroxy acids and polyhydric alcohols are linear.

05 Monomers comprising two groups containing reactive hydrogen atoms as aforesaid, for example di-carboxy or hydroxy substituted monomers may be utilised, especially as comonomers with cyclic(thio) ethers, epoxides or polyisocyanates, for example to produce polymers of the type disclosed in U.K. 1,572,598 and U.S. 4,221,779.

10 Examples of di-carboxy or hydroxy monomers include dicarboxylic acids, dihydric phenols, hydroxyacids, glycols and polyesters thereof, desirably those with less than 18, preferably less than 10, carbon atoms; for example oxalic, malonic, succinic, glutaric, and adipic acids, 1,2-cyclohexanedicarboxylic, 1,3-cyclohexanedicarboxylic and 1,4-cyclohexanedicarboxylic acids, phthalic, 15 isophthalic and terephthalic acids, 4,4'-dihydroxyphenyl-2,2-propane, resorcinol, quinol and orsinol, lactic, 2-hydroxyisobutyric, 10-hydroxydecanoic, 12-hydroxyoctadecenoic, 12-hydroxy-cis-9-octadecenoic, 2-hydroxycyclohexane carboxylic, 2-hydroxy-2-phenyl 20 (D) propionic, diphenylhydroxyacetic, 2-hydroxybenzoic, 3-hydroxybenzoic and 4-hydroxybenzoic acids, glycol, propanediols and butanediols. Glycols are most suitable, especially the C<sub>2</sub> to C<sub>6</sub>, preferably C<sub>2</sub> to C<sub>4</sub> glycols. Mixtures of dicarboxylic acids, dihydric phenols, hydroxy acids and glycols may be used. Preferably 25 the dicarboxylic acids, dihydric phenols, hydroxy acids and glycols are linear.

Cationic addition polymerisation in accordance with this invention requires acid catalysis. Suitable Bronsted and Lewis acids include strong mineral acids which are not redox reagents 30 under the reaction conditions such as hydrochloric and sulphuric acid, tosylic acid, brosylic acid and the adduct of methanol and boron trifluoride. Suitable Lewis acids include boron trifluoride and its etherate, boron tribromide, aluminium trichloride, aluminium tribromide, gallium trichloride, germanium tetrachloride, tin 35 tetrabromide, zinc chloride and ferric chloride, ferric chloride

being preferred. From 0.01% to 2%, particularly from 0.04% to 1%, based on the total weight of the reaction mixture may suitably be used.

05 In the case of the production of polyurethanes the, or one of the dihydroxy compounds may be a polyethylene oxide, preferably one wherein the ratio of number average weight to functionality is greater than 1000. The polyurethanes so produced are useful in the performance of the invention disclosed in GB.2047093 and GB.2047094.

10 It is the nature of the solvent, which may be a mixture of one or more compounds (including latent solvents) the composition of which may be varied, continuously or continually, as the polymerisation proceeds, which is a particularly critical feature of this invention. The solvent may qualitatively be assigned to one  
15 of three groups according to its hydrogen bonding capacity:

| <u>GROUP</u>               | <u>EXAMPLES</u>                                              |
|----------------------------|--------------------------------------------------------------|
| strongly hydrogen bonded   | alcohols, acids, amines, aldehydes                           |
| moderately hydrogen bonded | ketones, esters, ethers,                                     |
| poorly hydrogen bonded     | hydrocarbons, chlorinated and<br>nitrohydrocarbons, nitriles |

from which the meaning of "same or adjacent hydrogen bonding group" will be apparent.

20 The solubility parameter (which is the square root of the cohesive energy density) of a number of solvents is given in Table 1 below. In Table 2 solubility parameter ranges are given for a number of bulk polymers. (Both from "Encyclopaedia of Polymer Science and Technology" published by John Wiley & Sons.)

TABLE I

| <u>Solvents</u>            | <u>Solubility parameter</u> |
|----------------------------|-----------------------------|
| <u>Hydrocarbons</u>        |                             |
| aliphatic                  |                             |
| n-pentane                  | 7.05                        |
| isopentane                 | 7.05                        |
| n-hexane                   | 7.3                         |
| cyclohexane                | 8.2                         |
| n-heptane                  | 7.45                        |
| n-octane                   | 7.55                        |
| isooctane                  | 6.85                        |
| n-nonane                   | 7.65                        |
| n-decane                   | 7.75                        |
| n-tetradecane              | 7.95                        |
| butadiene                  | 6.7                         |
| isoprene                   | 7.25                        |
| aromatic                   |                             |
| benzene                    | 9.15                        |
| toluene                    | 8.9                         |
| o-xylene                   | 9.0                         |
| m-xylene                   | 8.8                         |
| p-xylene                   | 8.75                        |
| ethylbenzene               | 8.8                         |
| naphthalene                | 9.9                         |
| n-propylbenzene            | 8.65                        |
| isopropylbenzene           | 8.86                        |
| mesitylene                 | 8.8                         |
| p-cymene                   | 9.85                        |
| styrene                    | 8.66                        |
| <u>Perfluoro compounds</u> |                             |
| n-perfluorobutane          | 5.2                         |
| n-perfluoropentane         | 5.5                         |
| n-perfluorohexane          | 5.6                         |
| n-perfluoroheptane         | 5.7                         |
| n-perfluorononane          | 5.7                         |
| perfluorocyclobutane       | 5.7                         |
| perfluorocyclohexane       | 6.0                         |

TABLE I (continued)

| <u>Solvents</u>              | <u>Solubility parameter</u> |
|------------------------------|-----------------------------|
| <u>Perfluoro compounds</u>   |                             |
| perfluorobenzene             | 8.1                         |
| perfluorotoluene             | 7.7                         |
| <u>Halogen compounds</u>     |                             |
| <u>aliphatic chlorides</u>   |                             |
| dichloromethane              | 9.7                         |
| chloroform                   | 9.3                         |
| carbon tetrachloride         | 8.6                         |
| ethyl chloride               | 8.5                         |
| 1,1-dichloroethane           | 9.1                         |
| 1,2-dichloroethane           | 9.8                         |
| 1,1,1-trichloroethane        | 8.5                         |
| tetrachloroethane            | 10.4                        |
| isobutyl chloride            | 8.2                         |
| t-butyl chloride             | 7.9                         |
| <u>unsaturated chlorides</u> |                             |
| cis-dichloroethylene         | 9.7                         |
| trans-dichloroethylene       | 9.2                         |
| trichloroethylene            | 9.2                         |
| tetrachloroethylene          | 9.35                        |
| vinyl chloride               | 8.7                         |
| vinylidene chloride          | 8.6                         |
| chloroprene                  | 9.3                         |
| <u>aromatic compounds</u>    |                             |
| chlorobenzene                | 9.5                         |
| bromobenzene                 | 10.0                        |
| iodobenzene                  | 11.3                        |
| o-bromotoluene               | 9.8                         |
| <u>aliphatic bromides</u>    |                             |
| methyl bromide               | 9.4                         |
| bromoform                    | 10.5                        |
| ethyl bromide                | 8.9                         |
| 1,2-dibromoethane            | 10.4                        |

TABLE I (continued)

| <u>Solvents</u>           | <u>Solubility parameter</u> |
|---------------------------|-----------------------------|
| 1,1,2,2-tetrabromoethane  | 10.3                        |
| 1,2,3-tribromopropane     | 10.7                        |
| aliphatic iodides         |                             |
| methyl iodide             | 9.9                         |
| diiodomethane             | 11.8                        |
| ethyl iodide              | 9.4                         |
| <u>Hydroxyl compounds</u> |                             |
| water                     | 23.2                        |
| phenol                    | 14.5                        |
| glycol                    | 15.7                        |
| glycerol                  | 16.5                        |
| cyclohexanol              | 11.4                        |
| methanol                  | 14.5                        |
| ethanol                   | 12.7                        |
| n-propanol                | 11.9                        |
| n-butanol                 | 11.4                        |
| isobutyl alcohol          | 10.7                        |
| n-amyl alcohol            | 10.9                        |
| n-hexanol                 | 10.7                        |
| n-heptanol                | 10.0                        |
| n-octanol                 | 10.3                        |
| <u>Acids</u>              |                             |
| acetic acid               | 12.6                        |
| n-butyric acid            | 11.5                        |
| isovaleric acid           | 10.9                        |
| n-valeric acid            | 10.8                        |
| <u>Esters</u>             |                             |
| methyl formate            | 10.7                        |
| ethyl formate             | 9.4                         |
| methyl acetate            | 9.6                         |
| ethyl acetate             | 9.1                         |
| n-propyl acetate          | 8.75                        |

TABLE I (continued)

| <u>Solvents</u>        | <u>Solubility parameter</u> |
|------------------------|-----------------------------|
| isopropyl acetate      | 8.6                         |
| ethyl propionate       | 8.9                         |
| amyl formate           | 8.65                        |
| n-butyl acetate        | 8.55                        |
| ethyl n-butyrate       | 8.15                        |
| amyl acetate           | 8.45                        |
| butyl propionate       | 8.5                         |
| ethyl isovalerate      | 8.65                        |
| amyl propionate        | 8.4                         |
| n-butyl n-butyrate     | 8.0                         |
| isobutyl isobutyrate   | 7.7                         |
| isoamyl butyrate       | 8.5                         |
| ethyl benzoate         | 9.7                         |
| diethyl carbonate      | 8.8                         |
| diethyl malonate       | 10.3                        |
| ethylene carbonate     | 14.5                        |
| diethyl phthalate      | 10.05                       |
| vinyl acetate          | 8.7                         |
| methyl acrylate        | 8.9                         |
| ethyl acrylate         | 8.4                         |
| methyl methacrylate    | 8.7                         |
| ethyl methacrylate     | 8.4                         |
| n-butyl acrylate       | 8.9                         |
| n-butyl methacrylate   | 8.2                         |
| isobutyl methacrylate  | 7.9                         |
| <u>Aldehydes</u>       |                             |
| benzaldehyde           | 10.8                        |
| acetaldehyde           | 9.8                         |
| n-heptaldehyde         | 9.7                         |
| <u>Ketones</u>         |                             |
| acetone                | 10.0                        |
| methyl ethyl ketone    | 9.3                         |
| diethyl ketone         | 8.8                         |
| methyl n-propyl ketone | 8.7                         |

TABLE I (continued)

| <u>Solvents</u>          | <u>Solubility parameter</u> |
|--------------------------|-----------------------------|
| methyl n-butyl ketone    | 8.6                         |
| methyl amyl ketone       | 8.5                         |
| methyl hexyl ketone      | 8.45                        |
| cyclohexanone            | 9.9                         |
| <u>Ethers</u>            |                             |
| diethyl ether            | 7.4                         |
| diisopropyl ether        | 7.0                         |
| 1,1'-dichloroethyl ether | 9.8                         |
| dioxane                  | 10.0                        |
| tetrahydrofuran          | 9.9                         |
| <u>Amines</u>            |                             |
| di-n-butylamine          | 7.85                        |
| aniline                  | 10.8                        |
| pyridine                 | 10.7                        |
| <u>Amides</u>            |                             |
| formamide                | 17.8                        |
| acetamide                | 16.7                        |
| dimethylformamide        | 12.1                        |
| dimethylacetamide        | 11.1                        |
| <u>Nitriles</u>          |                             |
| acetonitrile             | 11.9                        |
| propionitrile            | 10.7                        |
| n-butyronitrile          | 10.5                        |
| n-valeronitrile          | 10.1                        |
| capronitrile             | 10.2                        |
| malonitrile              | 15.1                        |
| acrylonitrile            | 10.45                       |
| methacrylonitrile        | 9.1                         |
| <u>Nitro compounds</u>   |                             |
| nitromethane             | 12.6                        |
| nitroethane              | 11.1                        |
| 1-nitropropane           | 10.2                        |
| 2-nitropropane           | 9.9                         |

TABLE I (continued)

| <u>Solvents</u>         | <u>Solubility parameter</u> |
|-------------------------|-----------------------------|
| nitrobenzene            | 10.0                        |
| o-nitrotoluene          | 10.5                        |
| m-nitrotoluene          | 10.4                        |
| <u>Sulfur compounds</u> |                             |
| carbon disulfide        | 10.0                        |
| ethyl mercaptan         | 8.65                        |
| dimethyl sulfide        | 9.0                         |
| diethyl sulfide         | 8.8                         |
| thiophene               | 9.8                         |
| dimethyl sulfone        | 14.6                        |
| diethyl sulfone         | 12.5                        |
| dipropyl sulfone        | 11.3                        |
| dimethyl sulfoxide      | 13.4                        |

TABLE 2

| Polymers                           | Manufacturer | Solubility Parameter |               |           |
|------------------------------------|--------------|----------------------|---------------|-----------|
|                                    |              | Poor                 | Mod-<br>erate | Strong    |
| <u>Acrylics</u>                    |              |                      |               |           |
| acrylic solution polymers          |              |                      |               |           |
| Acryloid B-44                      | Rohm & Haas  | 8.9-11.9             | 8.5-13.3      | 0         |
| Acryloid B-66                      | Rohm & Haas  | 8.5-11.1             | 7.8-12.1      | 0         |
| Acryloid B-72                      | Rohm & Haas  | 8.5-12.7             | 8.9-13.3      | 0         |
| Acryloid B-82                      | Rohm & Haas  | 8.5-11.1             | 8.9-12.1      | 0         |
| poly(butyl acrylate)               | Rohm & Haas  | 7.0-12.7             | 7.4-12.1      | 9.5-12.7  |
| poly(methacrylic acid)             | Rohm & Haas  | 0                    | 9.9           | 12.7-14.5 |
| poly(methyl methacrylate)          | Rohm & Haas  | 8.9-12.7             | 8.5-13.3      | 0         |
| poly(ethyl methacrylate)           | Rohm & Haas  | 8.5-11.1             | 7.8-13.3      | 9.5-11.4  |
| poly(n-butyl methacrylate)         | Rohm & Haas  | 7.4-11.1             | 7.4- 9.9      | 9.5-11.4  |
| poly(isobutyl methacrylate)        | Rohm & Haas  | 8.5-11.1             | 8.5- 9.9      | 9.5-11.4  |
| <u>Alkyd resins</u>                |              |                      |               |           |
| 30% soy, glycerol phthalate        |              | 8.5-12.7             | 8.5-14.7      | 0         |
| 45% soy, glycerol phthalate        |              | 7.0-11.1             | 7.4-10.8      | 9.5-11.9  |
| 45% soy, pentaerythritol phthalate |              | 7.0-11.1             | 7.4-10.8      | 9.5-11.9  |
| 45% linseed, glycerol phthalate    |              | 7.0-11.9             | 7.4-10.8      | 9.5-11.9  |

TABLE 2 (continued)

| Polymers                                | Manufacturer       | Solubility Parameter |               |           |
|-----------------------------------------|--------------------|----------------------|---------------|-----------|
|                                         |                    | Poor                 | Mod-<br>erate | Strong    |
| <u>Epoxy resins</u>                     |                    |                      |               |           |
| bisphenol A-epichlorohydrin condensates |                    |                      |               |           |
| Epon E-72                               | Shell Chemical     | 8.5-10.6             | 7.4- 9.9      | 9.5-11.4  |
| Epon 812                                | Shell Chemical     | 8.9-12.7             | 7.8-14.7      | 10.0-14.5 |
| Epon 864                                | Shell Chemical     | 9.5-12.7             | 8.5-14.7      | 0         |
| Epon 1001                               | Shell Chemical     | 10.6-11.1            | 8.5-13.3      | 0         |
| Epon 1004                               | Shell Chemical     | 0                    | 8.5-13.3      | 0         |
| Epon 1007                               | Shell Chemical     | 0                    | 8.5-13.3      | 0         |
| Epon 1009                               | Shell Chemical     | 0                    | 8.5- 9.9      | 0         |
| <u>Hydrocarbon resins</u>               |                    |                      |               |           |
| cyclized rubber                         |                    |                      |               |           |
| Alpex cyclized rubber                   | Reichhold          | 7.4-10.6             | 7.8           | 0         |
| hydrocarbon resin                       |                    |                      |               |           |
| Gilsonite Brilliant Black               | American Gilsonite | 7.8-10.6             | 7.8- 8.5      | 0         |
| Gilsonite Selects                       | American Gilsonite | 7.8- 9.5             | 7.8- 8.5      | 9.5       |
| Nebony 100                              | Neville Chemical   | 8.5-10.6             | 7.8- 9.9      | 0         |
| Neville LX685                           | Neville Chemical   | 7.4-10.6             | 9.3- 9.9      | 0         |
| Panarez 3-210                           | Amoco Chemical     | 8.5-10.6             | 0             | 0         |

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TABLE 2 (continued)

| Polymers                      | Manufacturer     | Solubility Parameter |               |          |
|-------------------------------|------------------|----------------------|---------------|----------|
|                               |                  | Poor                 | Mod-<br>erate | Strong   |
| hydrocarbon resin (continued) |                  |                      |               |          |
| Petrolatum 125 IIMP           |                  | 8.5- 8.9             | 0             | 0        |
| natural rubber                |                  |                      |               |          |
| Pliolite NR                   | Goodyear         | 8.5-10.6             | 0             | 0        |
| Pliolite P-1230               | Goodyear         | 9.5-10.6             | 0             | 0        |
| <u>Phenolic resins</u>        |                  |                      |               |          |
| p-phenylphenol resin          |                  |                      |               |          |
| Bakelite CKR-5254             | Union Carbide    | 8.5-10.0             | 7.8-13.3      | 9.5-10.8 |
| phenolic resin                |                  |                      |               |          |
| Bakelite CKR-5360             | Union Carbide    | 8.5-11.1             | 7.8-13.3      | 9.5-11.4 |
| Bakelite CKR-2400             | Union Carbide    | 8.9-11.9             | 7.8-13.3      | 9.5-14.5 |
| Bakelite BKR2620              | Union Carbide    | 0                    | 8.4-14.7      | 9.5-14.5 |
| terpene-phenol resin          |                  |                      |               |          |
| Durez 220                     | Hooker Chemical  | 8.5-10.6             | 7.8- 9.8      | 9.5-11.4 |
| phenolic resin                |                  |                      |               |          |
| Durez 550                     | Hooker Chemical  | 7.0-11.9             | 7.4- 9.8      | 9.5-14.5 |
| phenol ether resin            |                  |                      |               |          |
| Methylon 75202                | General Electric | 0                    | 8.9-12.1      | 0        |

TABLE 2 (continued)

| Polymers                              | Manufacturer      | Solubility Parameter |               |          |
|---------------------------------------|-------------------|----------------------|---------------|----------|
|                                       |                   | Poor                 | Mod-<br>erate | Strong   |
| <u>Polyesters</u>                     |                   |                      |               |          |
| linear polyester                      |                   |                      |               |          |
| Vitel resin PE100-X                   | Goodyear          | 11.1                 | 9.9           | 0        |
| poly(ethylene terephthalate)          |                   |                      |               |          |
| soluble Mylar 49000                   | Du Pont           | 10.6-11.1            | 10.6-11.1     | 0        |
| soluble Mylar 49001                   | Du Pont           | 8.9-10.6             | 9.3- 9.9      | 0        |
| soluble Mylar 49002                   | Du Pont           | 9.5-10.6             | 9.3- 9.9      | 0        |
| <u>Amino resins</u>                   |                   |                      |               |          |
| urea-formaldehyde resin               |                   |                      |               |          |
| Beckamine P-196                       | Reichhold         | 9.9-11.1             | 8.5-10.8      | 9.5-12.7 |
| butylated urea-formaldehyde resin     |                   |                      |               |          |
| Beetle 227-8                          | American Cyanamid | 0                    | 0             | 8.9-11.4 |
| butylated melamine-formaldehyde resin |                   |                      |               |          |
| Resunene 888                          | Monsanto          | 8.5-10.6             | 7.4-12.1      | 9.5-12.7 |
| benzoguanamine-formaldehyde resin     |                   |                      |               |          |
| Uformite MX-61                        | Rohm & Haas       | 8.5-11.1             | 7.4-11.1      | 9.5-11.1 |

| Polymers                         | Manufacturer  | Solubility Parameter |               |           |
|----------------------------------|---------------|----------------------|---------------|-----------|
|                                  |               | Poor                 | Mod-<br>erate | Strong    |
| <u>Cellulose derivatives</u>     |               |                      |               |           |
| cellulose acetate, LL-1          |               | 11.1-12.7            | 9.9-14.7      | 0         |
| cellulose acetate butyrate       |               | 11.1-12.7            | 8.5-14.7      | 12.7-14.5 |
| cellulose butyrate, 0.5 sec      |               | 11.1-12.7            | 8.5-14.7      | 12.7-14.5 |
| cyanoethylcellulose              |               | 11.1-12.7            | 12.2-14.7     | 0         |
| ethylcellulose, K-200            |               | 0                    | 8.5-10.8      | 9.5-11.4  |
| ethylcellulose, N-22             |               | 8.1-11.1             | 7.4-10.8      | 9.5-14.5  |
| ethylcellulose, T-10             |               | 8.5- 9.5             | 7.8- 9.8      | 9.5-11.4  |
| cellulose nitrate, RS, 25 cps    |               | 11.1-12.7            | 7.8-14.7      | 14.5      |
| cellulose nitrate, SS, 0.5 sec   |               | 11.1-12.7            | 7.8-14.7      | 12.7-14.5 |
| <u>Polyamides</u>                |               |                      |               |           |
| methyldolpolyamide               |               |                      |               |           |
| nylon, type 8                    | Du Pont       | 0                    | 0             | 11.9-14.5 |
| dimer acid-polyamine condensates |               |                      |               |           |
| Versamid 100                     | General Mills | 8.5-10.6             | 8.5- 8.9      | 9.5-11.4  |
| Versamid 115                     | General Mills | 8.5-10.6             | 7.8- 9.9      | 9.5-12.7  |
| Versamid 900                     | General Mills | 0                    | 0             | 0         |
| Versamid 930                     | General Mills | 0                    | 0             | 9.5-11.4  |

TABLE 2 (continued)

| Polymers                                     | Manufacturer                 | Solubility Parameter |               |          |
|----------------------------------------------|------------------------------|----------------------|---------------|----------|
|                                              |                              | Poor                 | Mod-<br>erate | Strong   |
| dimer acid-polyamine condensates (continued) |                              |                      |               |          |
| Versamid 940                                 | General Mills                | 0                    | 0             | 9.5-11.4 |
| Versalon 1112                                | General Mills                | 0                    | 0             | 9.5-11.4 |
| Versalon 1175                                | General Mills                | 0                    | 0             | 9.5-11.4 |
| <u>Rosin derivatives</u>                     |                              |                      |               |          |
| WW gum rosin                                 |                              | 8.5-11.1             | 7.4-10.8      | 9.5-11.4 |
| wood rosin M grade                           |                              | 7.4-10.6             | 7.4-10.8      | 9.5-14.5 |
| ester gum                                    |                              | 7.0-10.6             | 7.4-10.8      | 9.5-10.9 |
| Alkydol 160                                  | Reichhold                    | 9.5                  | 8.5-10.8      | 9.5-12.7 |
| rosin-modified phenol-formaldehyde           |                              |                      |               |          |
| Amberol F-7                                  | Rohm & Haas                  | 8.5-10.6             | 7.8- 9.8-     | 9.5-10.9 |
| maleic rosin type                            |                              |                      |               |          |
| Amberol 750                                  | Rohm & Haas                  | 0                    | 8.9-10.8      | 9.5-12.7 |
| Amberol S01                                  | Rohm & Haas                  | 8.5-11.1             | 7.4- 9.9      | 0        |
| Arochem 455                                  | U.S. Industrial<br>Chemicals | 0                    | 7.8-13.3      | 9.5-14.5 |
| Arochem 462                                  | U.S. Industrial<br>Chemicals | 9.5                  | 8.5-10.8      | 9.5-14.5 |

TABLE 2 (continued)

| Polymers                                          | Manufacturer | Solubility Parameter |               |          |
|---------------------------------------------------|--------------|----------------------|---------------|----------|
|                                                   |              | Poor                 | Mod-<br>erate | Strong   |
| polymerized rosin                                 |              |                      |               |          |
| Dymerex                                           | Hercules     | 7.4-10.6             | 7.8- 9.9      | 9.5-11.4 |
| Nelio B952                                        | Glidden      | 9.5-10.6             | 7.4-10.8      | 9.5-12.7 |
| Nelio VBR757                                      | Glidden      | 0                    | 8.5-10.8      | 9.5-14.5 |
| rosin-derived alkyd                               |              |                      |               |          |
| Neolyn 23                                         | Hercules     | 8.5-11.1             | 8.5-13.3      | 0        |
| $\alpha$ -pinene resin                            |              |                      |               |          |
| Newport V-40                                      | Tenneco      | 8.5-11.1             | 7.4-12.1      | 9.5-14.5 |
| pentaerythrytol ester of rosin                    |              |                      |               |          |
| Pentalyn A                                        | Hercules     | 8.5-10.6             | 7.4- 9.9      | 9.5-11.4 |
| maleic-modified pentaerythrytol ester<br>of rosin |              |                      |               |          |
| Pentalyn G                                        | Hercules     | 8.5-10.6             | 7.8- 9.9      | 9.5-10.9 |
| pentaerythrytol ester of dimerized rosin          |              |                      |               |          |
| Pentalyn K                                        | Hercules     | 8.5-10.6             | 7.8- 9.9      | 9.5      |
| rosin-based polymers                              |              |                      |               |          |
| Pentalyn 830                                      | Hercules     | 8.5- 9.5             | 7.8-10.8      | 9.5-11.4 |
| Pentalyn 856                                      | Hercules     | 8.5-11.1             | 7.4-10.8      | 9.5-11.4 |
| Vinsol                                            | Hercules     | 10.6-11.9            | 7.8-13.3      | 9.5-12.7 |

TABLE 2 (continued)

| Polymers                                       | Manufacturer     | Solubility Parameter |          |           |
|------------------------------------------------|------------------|----------------------|----------|-----------|
|                                                |                  | Poor                 | Moderate | Strong    |
| <u>Styrene polymers and copolymers</u>         |                  |                      |          |           |
| <u>butadiene-styrene</u>                       |                  |                      |          |           |
| Buton 100                                      | Enjay            | 7.4-10.6             | 7.4- 9.9 | 0         |
| Buton 300                                      | Enjay            | 8.5-10.6             | 7.4- 9.9 | 9.5-10.5  |
| <u>styrene-maleic anhydride</u>                |                  |                      |          |           |
| Lytron 810                                     | Monsanto         | 11.9                 | 9.9-14.7 | 0         |
| Lytron 820                                     | Monsanto         | 9.5                  | 8.9-14.7 | 10.9-14.5 |
| <u>styrene copolymer</u>                       |                  |                      |          |           |
| Marbon 9200                                    | Marbon           | 8.5-10.6             | 9.3- 9.9 | 0         |
| <u>styrene-acrylonitrile-indene terpolymer</u> |                  |                      |          |           |
| Piccoflex 120                                  | Penn. Industrial | 8.5-11.1             | 7.8- 9.9 | 0         |
| <u>modified polystyrenes</u>                   |                  |                      |          |           |
| Styron 440M-27                                 | Dow              | 8.5-10.6             | 9.3      | 0         |
| Styron 475M-27                                 | Dow              | 8.5-10.6             | 9.3      | 0         |
| Styron 480-27                                  | Dow              | 9.5-10.6             | 9.3      | 0         |
| <u>rubber-modified polystyrene</u>             |                  |                      |          |           |
| Lustrex "High Test 88"                         | Monsanto         | 8.5-10.6             | 9.3      | 0         |
| Shell X-450                                    | Shell Chemical   | 9.5-10.6             | 8.5-12.1 | 9.5-12.7  |

TABLE 2 (continued)

| Polymers                          | Manufacturer  | Solubility Parameter |               |          |
|-----------------------------------|---------------|----------------------|---------------|----------|
|                                   |               | Poor                 | Mod-<br>erate | Strong   |
| styrene-acrylonitrile copolymer   |               |                      |               |          |
| Bakelite RMD4511 (S/An)           | Union Carbide | 10.6-11.1            | 9.3           | 0        |
| <u>Vinyl resins</u>               |               |                      |               |          |
| poly(vinyl chloride)              |               |                      |               |          |
| Exon 470                          | Firestone     | 8.5-11.1             | 7.8- 9.9      | 0        |
| Exon 471                          | Firestone     | 8.5-11.1             | 7.8-12.1      | 0        |
| Exon 473                          | Firestone     | 8.5-11.1             | 7.8- 9.9      | 0        |
| Geon 121                          | Goodrich      | 10.6-11.1            | 9.3- 9.9      | 0        |
| vinylidene chloride-acrylonitrile |               |                      |               |          |
| poly(vinyl butyl ether)           |               | 7.8-10.6             | 7.4- 9.9      | 9.5-11.4 |
| poly(vinyl ethyl ether)           |               | 7.0-11.1             | 7.4-10.8      | 9.5-14.5 |
| poly(vinyl formal)                |               |                      |               |          |
| Formvar 7/70E                     | Shawinigan    | 0                    | 9.9-13.3      | 0        |
| Formvar 15/95E                    | Shawinigan    | 0                    | 9.9-13.3      | 0        |
| poly(vinyl isobutyl ether)        |               | 7.0-10.6             | 7.4- 9.9      | 9.5-11.4 |

TABLE 2 (continued)

| Polymers                                                    | Manufacturer  | Solubility Parameter |               |          |
|-------------------------------------------------------------|---------------|----------------------|---------------|----------|
|                                                             |               | Poor                 | Mod-<br>erate | Strong   |
| vinylidene chloride-acrylonitrile copolymers                |               |                      |               |          |
| Saran F-120                                                 | Dow           | 9.5-11.1             | 12.1-14.7     | 0        |
| Saran F-220                                                 | Dow           | 9.5-11.1             | 10.8-14.7     | 0        |
| poly(vinyl acetate)                                         |               |                      |               |          |
| Vynlite AYAA                                                | Union Carbide | 8.9-12.7             | 8.5-14.7      | 14.5     |
| partially hydrolyzed vinyl chloride-vinyl acetate copolymer |               |                      |               |          |
| Vynlite VAGII                                               | Union Carbide | 10.6-11.1            | 7.8- 9.9      | 0        |
| vinyl chloride-vinyl acetate copolymer                      |               |                      |               |          |
| Vynlite VVIII                                               | Union Carbide | 10.6-11.1            | 7.8-12.1      | 0        |
| vinyl chloride-vinyl acetate-maleic acid terpolymer         |               |                      |               |          |
| Vynlite VMCH                                                | Union Carbide | 9.3-11.1             | 7.8-13.3      | 0        |
| vinyl chloride copolymer                                    |               |                      |               |          |
| Vynlite VXCC                                                | Union Carbide | 0                    | 8.9-10.8      | 9.5-14.5 |
| vinyl chloride-vinyl acetate copolymer                      |               |                      |               |          |
| Vynlite VYLF                                                | Union Carbide | 0                    | 8.9-10.8      | 9.5-14.5 |

TABLE 2 (continued)

| Polymers                        | Manufacturer  | Solubility Parameter |               |          |
|---------------------------------|---------------|----------------------|---------------|----------|
|                                 |               | Poor                 | Mod-<br>erate | Strong   |
| poly(vinyl butyral)             |               |                      |               |          |
| Vynlite XYHL                    | Union Carbide | 9.5-11.1             | 7.8-13.2      | 0        |
| Vynlite XYSG                    | Union Carbide | 9.5-11.1             | 7.8-13.2      | 0        |
| poly(ethylene-co-vinyl acetate) |               |                      |               |          |
| Elvax 150                       | Du Pont       | 7.8-10.6             | 0             | 0        |
| Elvax 250                       | Du Pont       | 8.5- 9.5             | 0             | 0        |
| Elvax EOD 3602-1                | Du Pont       | 7.8-10.6             | 7.8- 8.5      | 0        |
| <u>Miscellaneous</u>            |               |                      |               |          |
| synthetic oil                   |               |                      |               |          |
| Beckolin 27 (modified oil)      | Reichhold     | 7.0-11.1             | 7.4- 9.9      | 9.5-11.4 |
| poly(oxyethylene)glycol         |               |                      |               |          |
| Carbowax 4000                   | Union Carbide | 8.9-12.7             | 8.5-14.7      | 9.5-14.5 |
| chlorinated rubber              |               | 8.5-10.6             | 7.8-10.8      | 0        |
| hydrocarbon mixture             |               |                      |               |          |
| Conoco H-35                     | Conoco        | 7.0-11.1             | 7.4- 9.9      | 9.5-11.4 |
| dammar gum (dewaxed)            |               | 8.5-10.6             | 7.8- 9.9      | 9.5-10.9 |
| chlorosulfonated polyethylene   |               |                      |               |          |
| Hypalon 20                      | Du Pont       | 8.1- 9.8             | 8.4- 8.8      | 0        |

TABLE 2 (continued)

| Polymers                                                               | Manufacturer     | Solubility Parameter |               |           |
|------------------------------------------------------------------------|------------------|----------------------|---------------|-----------|
|                                                                        |                  | Poor                 | Mod-<br>erate | Strong    |
| chlorosulfonated polyethylene (continued)                              |                  |                      |               |           |
| Hypalon 30                                                             | Du Pont          | 8.5-10.6             | 7.8- 8.5      | 0         |
| phosgene-bisphenol A condensate                                        |                  |                      |               |           |
| polycarbonate Lexan 100, 105                                           | General Electric | 9.5-10.6             | 9.3-9.9       | 0         |
| arylsulfonamide-formaldehyde condensate                                |                  |                      |               |           |
| Santolite MHP                                                          | Monsanto         | 10.6-12.7            | 7.8-14.7      | 9.5       |
| shellac (pale-pale)                                                    |                  | 0                    | 9.9-10.8      | 9.5-14.5  |
| silicone polymers                                                      |                  |                      |               |           |
| Silicone DC-23                                                         | Dow-Corning      | 7.4- 8.5             | 7.4-7.8       | 9.5-10.0  |
| Silicone DC-1107                                                       | Dow-Corning      | 7.0- 9.5             | 9.9-10.8      | 9.5-11.4  |
| methoxylated partial hydrolyzate of<br>phenyl- and phenylmethylsilanes |                  |                      |               |           |
| Sylkyd 50                                                              | Dow-Corning      | 7.0-12.7             | 7.9-12.9      | 9.5-14.5  |
| monophenyl polysilaxanol                                               |                  |                      |               |           |
| Silicone Intermediate Z6018                                            | Dow-Corning      | 8.5-11.1             | 7.9-12.2      | 10.0-11.4 |
| soy oil                                                                |                  | 7.0-11.1             | 7.4-10.8      | 9.5-11.9  |
| soy oil, blown                                                         |                  | 7.0-11.1             | 7.4-10.8      | 9.5-12.7  |
| p-toluenesulfonamide-formaldehyde                                      |                  | 11.8                 | 9.9-14.7      | 12.7-14.5 |

In practice, an appropriate solvent for the performance of the present invention may readily be selected by first bulk polymerising the monomer mixture to a solid mass and then determining the swellability of portions of that mass in a number of  
05 solvents. Those solvents which swell it in excess of 100 pph of polymer will be suitable for the performance of the present invention, provided that they do not contain reactive groups which will interfere with the polymerisation. To obtain high molecular weight cross-linked particles which are capable of forming sols in  
10 the solvent, it is desirable to maintain a thermodynamically good solvent at all stages of the reaction.

Specific solvents whose use in the polymerisation of cyclic (thio)ethers and (meth)acrylate esters has been found desirable  
15 comprise one or more  $C_1$  to  $C_4$  alkyl acetates, especially methyl acetate and/or ethyl acetate. In the case of the polymerisation of epoxides or episulphides one or more halogenated hydrocarbons such as methylene chloride and/or chloroform were found very  
20 suitable. In the case of the polymerisation of polyisocyanates a mixture of one or more sulfoxides with one or more ketones, or chloroform, were found very suitable.

It is an important advantage of this invention that the polymerisation system does not require the presence, as is generally the case with non-aqueous dispersion or aqueous emulsion polymerisations, of an added stabiliser.

25 The polymerisation in accordance with this invention may be monitored, particularly at laboratory or pilot plant scale, by observing whether an aliquot of the reactant mixture spread onto a glass slide will form a coherent film. Provided that the solvent has been selected in the manner hereinbefore defined, the formation  
30 of coherent films occurs well before gelation.

When a coherent film is formed, or when other monitoring suggests, the polymerisation is terminated before gelation. For polymerisations which occur at elevated temperatures this may be achieved by cooling. Alternatively, polymerisation quenching  
35 agents may be added: base for cationic addition polymerisation;

weak acids for anionic addition polymerisation; and free radical traps such as alkylated phenolic or quinonoid inhibitors for free radical polymerisation.

According to a further aspect, this invention provides a  
05 polymeric material having a weight average molecular weight from 5,000 to 20,000,000 and comprising cross-linked particles which are capable of forming a sol whenever prepared by the process herein described. More particularly, this invention provides a polymeric  
10 material having a weight average molecular weight from 5,000 to 20,000,000 comprising particles of a homo- or copolymer of a substituted or unsubstituted (meth)acrylate ester cross-linked by a bis- or tris- vinyl or vinylidene group-containing ester which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material  
15 produced by bulk polymerising the monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer mixture, especially wherein the cross-linking ester comprises the bis-methacrylate ester of polyethylene glycol, the bis-methacrylate ester of ethylene glycol or triallyl  
20 cyanurate. This invention also provides a polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising cross-linked particles of a homo- or copolymer of a polymerisable cyclic (thio)ether which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$   
25 above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture, especially wherein the cyclic (thio)ether comprises acrolein tetramer. This invention further provides  
30 a polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising cross-linked particles of a homo- or copolymer of an epoxide or episulphide which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material  
35 produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture. This

invention also provides polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising cross-linked particles of a homo- or copolymer of a polyisocyanate which are capable of forming a sol in a solvent which (a) has a solubility parameter from 2.5 cal<sup>1/2</sup>ml<sup>-3/2</sup> below to 1.0 cal<sup>1/2</sup>ml<sup>-3/2</sup> above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture.

By selecting the solvent in accordance with this invention gelation, which in prior art processes rapidly follows the formation of the aforesaid cross-linked, sol-forming particles, is delayed for a sufficient period to enable the termination to be effected in a controlled manner. The sol-forming particles so produced have a very small particle size in the colloidal or sub-colloidal size range; that is an average primary particle size no greater than 0.2 $\mu$ .

The reacted solutions so formed can either be used as such, in concentrated form, or the polymer can be recovered. Recovery can be effected by solvent evaporation or mixing, either by addition or reverse addition, with an excess of a non-solvent. A particularly desirable feature of the invention is that the polymer produced by addition of excess non-solvent is typically a flowable powder, generally of fine particle size. Moreover, the polymer powder can readily be redissolved in the same or other solvent selected in accordance with this invention. It is believed that the polymer particles are globular when in solution and it is found that they typically contribute little to the viscosity of the solution until their swollen phase volume exceeds a critical fraction of the whole which, in practice, means that the polymer solution can be concentrated to about 20%, and sometimes to about 30%, by weight and still be readily pourable.

The polymer powders of this invention are useful as industrial and pharmaceutical compression moulding materials. They may be used in admixture with an active substance; for example, a pharmaceutical, bacteriostat, viruscide, insecticide, herbicide, larvicie, fungicide,

algaeicide, nematocide, topical or dermatological agent, antifoulant for marine growth prevention, enzyme, preservative, fluorescent or other pigment. The polymer powders of this invention are particularly useful as pharmaceutical tableting excipients, especially as direct  
05 compression tableting excipients. This is particularly the case for polymers prepared from cyclic (thio)ethers, such as acrolein tetramer. The active substance may be incorporated by admixing solid active substance, for example pharmaceutical or pigment, for example before tableting or the active substance may be added to a solution of the polymer,  
10 coprecipitated therewith and then tableted. In the latter case the swollen sol particles permit the active substance to penetrate the polymer network. The polymer powders are also useful as additives for bulk rubbers, sound damping formulations, viscosity control additives.

This invention also provides a polymeric material as herein defined  
15 which is dissolved in a solvent which is different from the reaction solvent. This solvent may comprise one or more monomers which may be reactive with the polymeric material. Desirably, at least one of the monomers is a (meth)acrylate ester, styrene, alkyl styrene, vinyl chloride or acrylonitrile.

20 This invention also provides a surface coating composition such as an adhesive paint, varnish or lacquer, especially alkyl and acrylic based surface coatings, which comprise a polymeric material, which may comprise pigment introduced as aforesaid, especially one in a solvent which is different from the reaction solvent as aforesaid. This invention further  
25 provides a cured such surface coating composition; such materials typically have a reduced drying time, generate less heat and reduce shrinkage. It is to be noted that even if the solvent monomers do not interpolymerise with the polymeric material of this invention they will penetrate the polymer network and their resultant homopolymers will bind the polymer  
30 particles by entanglement.

The following Examples illustrate the invention; in each Example the solubility parameter of the solvent is from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture.

#### EXAMPLE 1

35 1.9241g (0.0086 mols) of acrolein tetramer were added to 0.5379g (0.0057 mols) of glycerol containing 2% by weight of  $\text{FeCl}_3$

in a reaction vessel equipped with a nitrogen bleed and a drying tube to exclude moisture. 3.30cm<sup>3</sup> of methyl acetate were added to form a mixture which, initially, was not homogeneous. The mixture was continuously stirred and heated on a water bath whereupon it became homogeneous after about 15 minutes and was permitted to reflux.

Aliquots of the reactant mixture spread onto a slide began to produce solid film after 70 minutes from the beginning of reflux. The solution was then neutralised with triethylamine after 73 minutes of reaction,  $1.3 \times 10^{-4}$  mols of triethylamine being required for the neutralisation.

The concentration of polymer in the solution was 8.2% by weight. It was possible to concentrate the polymer solution after neutralisation to about 24% by weight by distilling the excess methyl acetate or by using a rotary evaporator.

Polymer powder was obtained from the solution either by a film spreading technique or by precipitating the polymer solution by gradual addition to an excess of hexane.

#### EXAMPLE 2

1.9876g (0.0089 mol) of acrolein tetramer were added to 1.0703g (0.012 mol) of glycerol containing 2% by weight of FeCl<sub>3</sub>, in a reaction vessel equipped as in Example 1. 4cm<sup>3</sup> of methyl acetate were added to form a mixture which became homogeneous after about 15 minutes of stirring and heating. The mixture was refluxed for one hour then a further amount (1.91889g; 0.0086 mols) of acrolein tetramer was added, along with 56 mol of methylene chloride so that the ratio methyl acetate : methylene chloride was approximately 7 : 93 by volume and the ratio acrolein tetramer : glycerol was 3 : 2. The refluxing was continued and after 90 minutes from commencing refluxing a film began to form when the solution was spread on a glass slide. The mixture was neutralised after 100 minutes by adding triethylamine.

The concentration of polymer in the solution was 8.3% by weight. The polymer solution could be concentrated to about 24% by weight either by distillation or using a rotary evaporator.

algaeicide, nematocide, topical or dermatological agent, antifoulant for marine growth prevention, enzyme, preservative, fluorescent or other pigment. The polymer powders of this invention are particularly useful as pharmaceutical tableting excipients, especially as direct compression tableting excipients. This is particularly the case for polymers prepared from cyclic (thio)ethers, such as acrolein tetramer. The active substance may be incorporated by admixing solid active substance, for example pharmaceutical or pigment, for example before tableting or the active substance may be added to a solution of the polymer, coprecipitated therewith and then tableted. In the latter case the swollen sol particles permit the active substance to penetrate the polymer network. The polymer powders are also useful as additives for bulk rubbers, sound damping formulations, viscosity control additives.

This invention also provides a polymeric material as herein defined which is dissolved in a solvent which is different from the reaction solvent. This solvent may comprise one or more monomers which may be reactive with the polymeric material. Desirably, at least one of the monomers is a (meth)acrylate ester, styrene, alkyl styrene, vinyl chloride or acrylonitrile.

This invention also provides a surface coating composition such as an adhesive paint, varnish or lacquer, especially alkyl and acrylic based surface coatings, which comprise a polymeric material, which may comprise pigment introduced as aforesaid, especially one in a solvent which is different from the reaction solvent as aforesaid. This invention further provides a cured such surface coating composition; such materials typically have a reduced drying time, generate less heat and reduce shrinkage. It is to be noted that even if the solvent monomers do not interpolymerise with the polymeric material of this invention they will penetrate the polymer network and their resultant homopolymers will bind the polymer particles by entanglement.

The following Examples illustrate the invention; in each Example the solubility parameter of the solvent is from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture.

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30 from commencing refluxing a film began to form when the solution was spread on a glass slide. The mixture was neutralised after 100 minutes by adding triethylamine.

The concentration of polymer in the solution was 8.3% by weight. The polymer solution could be concentrated to about 24%  
35 by weight either by distillation or using a rotary evaporator.

Polymer powder was obtained as described in Example 1.

Using essentially the same preparative technique, copolymers with acrolein tetramer : glycerol weight ratios 70 : 30, 72 : 28, 74 : 26 and 76 : 24 were also prepared. These copolymers usually had lower molecular weights than the 3 : 2 copolymer produced in this and Example 1 above.

### EXAMPLE 3

The preparation was carried out in two stages:

(a) Master batch preparation:

10 A master batch of citric acid and acrolein tetramer in ethyl acetate was prepared for use in the preparation of citric acid acrolein tetramer copolymer. The ratio acrolein tetramer : citric acid in the master batch was stoichiometric (2 mols of acrolein tetramer to 1 mol of citric acid on the assumption that the three  
15 carboxylic groups and one hydroxyl group in citric acid would react). 35.0965g (0.1567 mols) of acrolein tetramer were added to 15.0506g citric acid (0.0783 mols), and the mixture was then added to 450cm<sup>3</sup> of ethyl acetate.

The mixture was next placed in a round-bottom flask and  
20 refluxed with continuous stirring under a nitrogen bleed. The refluxing and stirring was stopped after half an hour to provide a homogeneous prepolymer which formed only a low molecular weight tacky film. The notional concentration of acrolein tetramer and citric acid was 10% w/v.

25 (b) Preparation of the copolymer:

200cm<sup>3</sup> of methylene chloride were added to 100cm<sup>3</sup> of the master batch together with 10cm<sup>3</sup> of 0.3% FeCl<sub>3</sub> solution in methylene chloride. The contents were then stirred at room temperature. After 30 minutes the mixture became cloudy and a solid film-producing  
30 solution was formed. The reaction was then terminated by adding triethylamine after one hour of stirring in both stages (a) and (b) combined. Soon after the addition of triethylamine the mixture became very cloudy.

The polymer concentration was 3.5% w/v and could be concentrated  
35 to about 10% w/v using a rotary evaporator.

Polymer powder was obtained by precipitation by gradually adding the solution to an excess of hexane.

EXAMPLE 4

Copolymers of acrolein tetramer/citric acid/glycerol of different ratios were prepared.

(a) The following procedure was used for the preparation of copolymers with weight ratios of 78:11:11, 78:9:13, 78:7:15 and 78:2:20 of acrolein tetramer/citric acid/glycerol. A similar procedure could be used for other ratios.

1.17g of acrolein tetramer were added to 0.5g of anhydrous citric acid and 0.5g glycerol containing 2% by weight of  $\text{FeCl}_3$  in a reaction vessel equipped with a nitrogen bleed and a drying tube to exclude moisture. 20cm<sup>3</sup> of ethyl acetate were added to form a mixture which, initially, was not homogeneous. The mixture was

continuously stirred and heated on a water bath whereupon it became homogeneous after about half an hour and was permitted to reflux. After one hour of refluxing a further 2.38g of acrolein tetramer were added together with 30cm<sup>3</sup> methylene chloride. The ratio of acrolein tetramer to the other components was thus 78%.

After 30 minutes refluxing after the second addition, the solution was film-forming. The solution was then neutralised by adding a few drops of triethylamine. The concentration of the polymer in the solution was 9% w/v. Polymer powder was obtained by precipitation by adding excess hexane.

(b) Copolymers of acrolein tetramer/citric acid/glycerol with ratios of 78:13:9, 78:15:7 and 78:20:2 were prepared by using the following procedure.

1.00g of acrolein tetramer was added to 0.41 glycerol containing 2% by weight  $\text{FeCl}_3$  and 0.59g of anhydrous citric acid in a reaction vessel equipped with a nitrogen bleed and a drying tube to exclude moisture. 50cm<sup>3</sup> ethyl acetate were added to form a mixture which, initially, was not homogeneous. The mixture was continuously stirred and heated on a water bath whereupon it became homogeneous after about 10 minutes and was permitted to reflux. After 25 minutes of refluxing a further 2.55g of acrolein tetramer were added, along

with 25cm<sup>3</sup> methylene chloride and 0.4cm<sup>3</sup> 0.3% ferric chloride solution in methylene chloride. The ratio of acrolein tetramer to the other components was thus 78% of the total content of acrolein tetramer/citric acid/glycerol. After 10 minutes refluxing after  
05 the second addition the mixture was film-forming. The solution was then neutralised with triethylamine.

Polymer powder was obtained by precipitation by adding excess hexane. By using the above procedure, copolymers of acrolein tetramer/citric acid/glycerol with a higher content of citric acid  
10 than glycerol were prepared, provided that the necessary additional amount of ferric chloride was added in the second stage.

#### EXAMPLE 5

2.24g of acrolein tetramer (0.01 mol) and 10.0cm<sup>3</sup> of a 0.1% FeCl<sub>3</sub> solution in methyl acetate were mixed in a reaction vessel.  
15 The concentration of acrolein tetramer in the solution was 22 wt. %. The mixture was then allowed to react at a temperature of 20°C and after 65 minutes a turbid solution was formed. After 70 minutes 1.14cm<sup>3</sup> (0.02 mol) of ethanol as added to terminate the polymerisation.

20 After the addition of the alcohol, the mixture was refluxed for a further 15 minutes to produce a slightly turbid low viscosity solution. The solution, spread on a glass microscope slide, produced a continuous solid dry polymeric film.

Polymer powder was obtained by adding excess alcohol or  
25 hexane to the solution.

#### EXAMPLES 6 TO 8

The materials used in these three Examples were:

- (a) a cycloaliphatic epoxy resin (Trade Mark CY179, 3M Company);
- (b) epoxy curing agent FC503 (Trade Mark, 3M Company);
- 30 (c) the polymer, in solution in methyl acetate, produced according to Example 5.

The three components were admixed, in the proportions by weight given in the Table below, and the methyl acetate was evaporated off in the dark in an oven with forced ventilation. The  
35 resulting materials were golden yellow in colour.

TABLE 3

| <u>Example No.</u>       | <u>6</u> | <u>7</u> | <u>8</u> |
|--------------------------|----------|----------|----------|
| FC503                    | 10       | 10       | 10       |
| Microparticulate polymer | 20       | 30       | 40       |
| CY179                    | 70       | 60       | 50       |
|                          | <hr/>    | <hr/>    | <hr/>    |
|                          | 100      | 100      | 100      |
|                          | <hr/>    | <hr/>    | <hr/>    |

The products were coated as thin films on an aluminium sheet and were found to cure rapidly to a tack-free, scratch-resistant film after one passage under a U.V. lamp in a line travelling at 300 feet per minute.

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EXAMPLE 9

Diglycidylether of bisphenol known as Epikote (Trade Mark) 828 was used to prepare a crosslinked sol in methylene chloride solution.

10  $5\text{cm}^3$  of  $\text{BF}_3$  solution was added to a mixture of  $100\text{cm}^3$  30% Epikote 828 solution and  $750\text{cm}^3$  of methylene chloride. Polymerisation was effected at room temperature under a nitrogen atmosphere for 3 hours, during which time the solution became more viscous. The mixture was film-forming after 20 minutes and was neutralised, with triethylamine, after 3 hours of polymerisation.

15 Various polymers based on Epikote 828 were prepared using the above procedure but altering the polymerisation time from 1 hour to 5 hours. The  $\text{BF}_3$  solution was prepared by diluting  $\text{BF}_3$  methanol solution to a 45% solution with methylene chloride. The Epikote 828 solution was prepared in methylene chloride.

20 At the end of the polymerisation, the polymer concentration was 6.5% w/v. However, it was possible to concentrate the solution by using a rotary evaporator while avoiding heating. It was possible to achieve 16% polymer solution without affecting its stability. Polymer powder was obtained by precipitation by adding  
25 excess hexane, slowly with continuous stirring. The polymer powder could be readily dispersed again in methylene chloride.

EXAMPLE 10

Polyethylene glycol 6000 (ex ICI) and trimethylol propane were dried under vacuum for 1 hour at 70°C. Diphenylmethane-4, 4'-diisocyanate (MDI) was distilled under reduced pressure and used immediately.

Polyethylene glycol 6000 (10g) was placed in a 250cm<sup>3</sup> glass flask equipped with stirrer, nitrogen bleed, condenser and CaCl<sub>2</sub> drying tube to exclude moisture with a mixture of dimethylsulphoxide and methyl ethyl ketone in a weight ratio of 1 : 1 (50g) and heated to 70°C. MDI (1.15g) was then added followed, after 5 minutes, by trimethylol propane (0.27g). The mixture was next heated at 80 - 100°C for 5 hours by which time no infra-red isocyanate absorption band at 2275nm could be detected and polymer solution had formed.

Polymer powder was obtained by slowly adding the polymer solution to an excess of cyclohexane or petrol ether (60/80) followed by filtration and drying in a vacuum oven at room temperature.

The powder so formed would readily redisperse to a stable system in either 1 : 1 dimethylsulphoxide/methyl isobutyl ketone or into water.

The dispersion in water had the interesting characteristic of being clear at room temperature but of milky appearance at 100°C. The dispersion is useful as a thickener in water as it can provide very viscous dispersions at room temperature which show a remarkable reduction in viscosity at elevated temperature.

EXAMPLE 11

3.89g of triallyl cyanurate was added to 105cm<sup>3</sup> of methyl methacrylate in a round bottom flask heated in a heating mantle. These were stirred together with 5.00cm<sup>3</sup> ethyl acetate under a nitrogen atmosphere for 20 minutes followed by the addition of 5ml of 7% benzoyl peroxide solution. Refluxing and stirring was continued under a nitrogen atmosphere for 5 hours. After 5 hours polymerisation the mixture was cooled to room temperature. Polymer powder was obtained by precipitation by adding the polymer solution gradually to excess methanol.

The molar ratio methyl methacrylate : triallyl cyanurate was 64 : 1. The polymer solution concentration was 20%.

Using the above procedure, other molar ratios of copolymers were prepared from 5 : 1 to 1 : 4.

EXAMPLE 12

A mixture of 21.26cm<sup>3</sup> methyl methacrylate, 41.56cm<sup>3</sup> ethyl hexacrylate and 15.08 polyethylene glycol 600 dimethacrylate in 600cm<sup>3</sup> ethyl acetate was allowed to stand under a nitrogen atmosphere for 20 minutes. 2cm<sup>3</sup> of 7% benzoyl peroxide solution were then added. Refluxing and stirring were next carried out in a round bottom flask in a heating mantle under a nitrogen atmosphere for 5 hours. After 5 hours copolymerisation, the solution was cooled to room temperature. The copolymer formed from this mixture at this stage was rubbery. The molar ratio methyl methacrylate : 2-ethyl hexyl acrylate : polyethylene glycol 600 dimethacrylate was 2 : 2 : 1. The concentration of the solution was about 10% w/v. It was possible to concentrate the solution to about 25% w/v by evaporation of the solvent.

Other copolymers with different molar ratios of components could be prepared by using the above procedure, although catalyst and solvent concentration may need to be altered, e.g. copolymer of molar ratio methyl methacrylate : 2-ethylhexyl acrylate : polyethylene glycol 600 dimethacrylate of 2 : 2 : 2 was prepared using 1cm<sup>3</sup> of 7% benzoyl peroxide solution. The polymer solution concentration was about 7% w/v. This extra amount of solvent was necessary to avoid gelation during the process.

EXAMPLE 13

Benzoyl peroxide was added to a solution of methyl methacrylate and triallyl cyanurate (mol ratio 64 : 1) in ethyl acetate and the reaction mixture was refluxed under a nitrogen atmosphere with stirring for 5 hours. The concentration of the polymer solution was 20% by weight. The polymer solution was added slowly, with continuous stirring, to methanol to precipitate the polymer which was filtered and dried to give a powder.

EXAMPLE 14

Example 13 was repeated using a ratio of 20 : 1. At the end of the 5 hour reaction period the polymer was recovered by precipitation in methanol, filtration and drying.

05

EXAMPLE 15

Benzoyl peroxide was added to a solution of methyl methacrylate, 2-ethyl hexylacrylate and polyethylene glycol 600 dimethacrylate (mol ratio 2 : 2 : 1,) in ethyl acetate and the reaction mixture was stirred continuously under reflux in a nitrogen atmosphere for 10 5 hours to give a polymer solution. The total polymer concentration in the ethyl acetate was 10% by weight.

EXAMPLE 16

1.3310g of triallyl cyanurate (ex BDH, used without further purification) and 6.85g of methyl methacrylate (molar ratio 1 : 12, 15 respectively) were mixed with 81.8cm<sup>3</sup> of ethyl acetate (ex Fisons, dried over MgSO<sub>4</sub> and distilled before use) in a round bottom flask equipped with a nitrogen bleed and a drying tube to exclude moisture. The solution so formed was purged with oxygen-free nitrogen for 20 minutes. The solution was then heated and stirred with a mantle 20 cum stirrer. When reflux commenced 5.0cm<sup>3</sup> of a 7% by weight solution of benzoyl peroxide, as catalyst, in ethyl acetate were added. Heating was discontinued after 3½ hours of refluxing when a polymer film was observed to form in the flask. The polymer was precipitated as a fine white powder by addition of excess diethyl 25 ether to the solution. 82% conversion was obtained.

EXAMPLE 17

2.8770g of triallyl cyanurate and 23.11g of methyl methacrylate (molar ratio 1 : 20, respectively) were mixed with 280cm<sup>3</sup> of ethyl acetate (initial monomer concentration 10% w/v), and reacted 30 essentially as described in Example 16. After 3¾ hours of refluxing a slight haze, but no polymer film, was observed in the flask. Heating was discontinued and the polymer precipitated as described in Example 16. 51% conversion was obtained.

EXAMPLE 18

35 3.6267g of triallyl cyanurate and 46.613g of methyl methacrylate (molar ratio 1 : 64, respectively) were mixed with 525cm<sup>3</sup> of ethyl

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acetate in a three-necked, round bottom flask equipped with a condenser, drying tube, nitrogen bleed and a self-sealing rubber septum. The solution so formed was purged with oxygen-free nitrogen for 20 minutes. The solution was then heated and stirred with a mantle cum stirrer. When reflux commenced, 5.0cm<sup>3</sup> of a 7% by weight solution of benzoyl peroxide, as catalyst, in ethyl acetate were added. While the reactant mixture was polymerising its polymer content was estimated, at about every 30 minutes, by syringing out 1.0cm<sup>3</sup> aliquots of reactant mixture; accurately weighing them; adding them to a clean, dry preweighed aluminium dish; and evaporating to dryness by heating in an oven at 100°C for 30 minutes. The percentage conversion was then estimated from a set of three such measurements.

After 5½ hours another 5.0cm<sup>3</sup> shot of catalyst was added and polymer content was continually measured, as aforesaid, until the solids content after evaporating to dryness remained unaltered in two consecutive determinations. At this time the reaction had been in progress for 13½ hours. Thereafter a final 5.0cm<sup>3</sup> shot of catalyst was added and reflux maintained for a total reaction time of 14½ hours, by which time a conversion of 98.8% was estimated.

Petroleum ether (ex Koch-Light b.p. 80 - 100°C) was next added dropwise to the stirred reacted mixture until it became hazy. This hazy solution was then added dropwise to a large excess of petroleum ether which was maintained vigorously stirred. The polymer precipitated as a fine white powder which was filtered and dried overnight in vacuo.

#### EXAMPLE 19

2.0257g of the polymer prepared in Example 18 were placed in a clean quickfit test tube to which 6.692g of methyl acrylate (ex BDH, distilled under vacuum) were added. The tube was then securely stoppered and shaken for 10 minutes after which 0.005g of benzil (ex Fisons Scientific Apparatus Ltd., recrystallised from absolute alcohol), as initiator, was added. Shaking was next continued for a further 3 minutes whereafter the mixture was allowed to stand for a further 5 minutes to give a 23.2% w/w solution of the polymer.

Aliquots were then polymerised to form a film of 3 thou thickness between two clear glass plates sealed by a rubber gasket by placing in U.V. radiation for 12 hours.

EXAMPLE 20

05           2.3760g of the polymer prepared in Example 18 were dissolved  
in 7.488g of methyl methacrylate (ex BDH, distilled under vacuum)  
containing 0.0063g of azobisisobutyronitrile (ex Eastman Chemicals  
Limited, recrystallised from absolute alcohol) as initiator. The  
10 clear solution so formed was polymerised for 6 hours in the manner  
described in Example 19.

A very clear film with a smooth surface was formed which was brittle on scratch but resistant, up to 40 passes, to the solvent action of an acetone-damped cloth.

EXAMPLE 21

15           In essentially the same procedure as Example 20, 3.3530g of  
the polymer of Example 18 were dissolved in 6.552g of methyl  
methacrylate and polymerised using 0.007g of benzil as initiator.

EXAMPLE 22

20           3.8660g of the polymer prepared in Example 18 were dispersed  
in 6.468g of ethyl acrylate (ex BDH, distilled under vacuum) in a  
test tube to which 0.0502g of azobisisobutyronitrile was added. The  
tube was then shaken for 5 minutes forming a 37.4% w/w solution of the  
polymer which was photopolymerised for 5 hours in the manner described  
in Example 19.

EXAMPLE 23

25           6.0g of the polymer prepared in Example 18 were dispersed, in stages,  
in 4.62g of ethyl acrylate in a test tube to which 0.014g of benzil was  
added. The tube was then vigorously shaken until a clear solution (which  
was viscous but still pourable) was obtained. The tube was next treated  
30 with sonic energy to remove air bubbles entrapped during shaking and the  
solution was photopolymerised for 16 hours in the manner described in  
Example 19.

35           ("GILSONITE", "PLIOLITE", "BAKELITE", "DUREZ", "UITEL", "MYLAR",  
"BEETLE", "LLFORNITE", "VERSAMID", "VERSALON", "NELIO", "PENTALYN", "LYTRON",  
"STYRON", "LUSTREX", "GEON", "FORMVAR", "SARAN", "VINYLITE", "ELVAX",  
"CARBOWAX", "CONOCO", "HYPALON", "LEXAN", "SANTOLITE" and "QUICKFIT" are  
registered Trade Marks.)



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CLAIMS

1. A solution polymerisation process for the preparation of a polymeric material having a weight average molecular weight from 5,000 to 20,000,000 and comprising cross-linked particles which are capable of forming a sol in the reaction solvent, which process comprises:
  - (i) polymerising one or more monomers, the or at least one of which is a cross-linking agent, in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture;
  - (ii) monitoring the polymerisation until polymeric material as herein defined is obtained; and
  - (iii) terminating the polymerisation before gelation is obtained.
2. A process according to Claim 1 wherein the polymerisation is an addition polymerisation.
3. A process according to Claim 2 wherein the polymerisation is a cationic addition polymerisation.
4. A process according to Claim 3 wherein the, or one of the, monomers comprises a polymerisable cyclic (thio)ether.
5. A process according to Claim 4 wherein the cyclic (thio)ether comprises acrolein tetramer.
6. A process according to Claim 2 wherein the polymerisation is a free radical addition polymerisation.
7. A process according to Claim 6 wherein the, or one of the, monomers comprises a vinyl or vinylidene group-containing monomer.
8. A process according to Claim 7 wherein the vinyl or vinylidene group-containing monomer comprises a substituted or unsubstituted (meth)acrylate ester.
9. A process according to Claim 8 wherein the substituted or unsubstituted (meth)acrylate ester comprises a  $C_1$  to  $C_8$  alkyl methacrylate.
10. A process according to any of Claims 6 to 9 wherein a bis- or tris-vinyl or vinylidene group-containing monomer is present as a cross-linking agent.



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11. A process according to Claim 10 wherein the cross-linking agent comprises a bis- or tris- vinyl or vinylidene group-containing ester.
12. A process according to Claim 11 wherein the ester comprises the bis-methacrylate ester of polyethylene glycol, the bis-methacrylate ester of ethylene glycol or triallyl cyanurate.
13. A process according to any of Claims 2 to 5 wherein the, or one of the, monomers comprises an epoxide or episulphide.
14. A process according to Claim 1 wherein the polymerisation is a condensation polymerisation.
15. A process according to Claim 14 wherein the, or one of the, monomers comprises a polyisocyanate.
16. A process according to any of Claims 2 to 5, 13, 14 or 15 wherein a monomer comprising at least three groups which are hydroxyl and/or carboxyl groups is present as cross-linking agent.
17. A process according to any of Claims 4, 5 and 8 to 12 wherein the solvent comprises one or more  $C_1$  to  $C_4$  alkyl acetates.
18. A process according to Claim 13 wherein the solvent comprises one or more halogenated hydrocarbons.
19. A process according to Claim 15 wherein the solvent comprises a mixture of one or more sulfoxides with one or more ketones.
20. A polymeric material having a weight average molecular weight from 5,000 to 20,000,000 and comprising cross-linked particles which are capable of forming in sol whenever prepared by the process of any of Claims 1 to 19.
21. A polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising particles of a homo- or copolymer of a substituted or unsubstituted (meth)acrylate ester cross-linked by a bis- or tris- vinyl or vinylidene group-containing ester which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility of the material produced by bulk polymerising the monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer mixture.
22. A polymeric material according to Claim 21 wherein the cross-linking ester comprises the bis-methacrylate ester of polyethylene



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glycol, the bis-methacrylate ester of ethylene glycol or triallyl cyanurates.

23. A polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising cross-linked particles of a homo- or copolymer of a polymerisable cyclic (thio)ether which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture.

24. A polymeric material according to Claim 23 wherein the cyclic (thio)ether comprises acrolein tetramer.

25. A polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising cross-linked particles of a homo- or copolymer of an epoxide or episulphide which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture.

26. A polymeric material having a weight average molecular weight from 5,000 to 20,000,000 comprising cross-linked particles of a homo- or copolymer of a polyisocyanate which are capable of forming a sol in a solvent which (a) has a solubility parameter from  $2.5 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  below to  $1.0 \text{ cal}^{1/2} \text{ ml}^{-3/2}$  above the solubility parameter of the material produced by bulk polymerising the monomer or monomer mixture and (b) is of the same or adjacent hydrogen bonding group as the material produced by bulk polymerising the monomer or monomer mixture.

27. A polymeric material according to any of Claims 23 to 26 wherein a monomer comprising at least three groups which are hydroxyl and/or carboxyl groups is present as cross-linking agent.

28. A polymeric material according to any of Claims 20 to 27 which is a flowable powder.

29. A compression moulding material according to Claim 28.

30. A moulding material according to Claim 29 which is a pharmaceutical tableting excipient.

31. A pharmaceutical tableting excipient according to Claim 30 which is a direct compression excipient.



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32. A polymeric material according to any of Claims 20 to 27 which is dissolved in a solvent which is different from the reaction solvent.
- 05 33. A polymeric material according to Claim 32 wherein the solvent is one or more monomers reactive with polymeric material.
34. A polymeric material according to Claim 33 wherein at least one of the monomers is a (meth)acrylate ester.
35. A surface coating composition which comprises a polymeric material according to any of Claims 32 to 34.
- 10 36. A cured polymeric material according to any of Claims 32 to 35.
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