

Description

This invention relates to the anionic polymerization of alkyl methacrylate monomers and in particular to the pretreatment of the alcohol containing starting monomer.

Alkyl methacrylates may be polymerized by either anionic or free radical mechanisms. A problem with free radical polymerization is termination of the polymerization by disproportionation or by combination reactions. These untimely terminations of the polymer growth cause free radically polymerized polymers to have broad molecular weight distributions. These termination mechanisms and other limitations associated with free radical polymerization also prevent preparation of well defined block copolymers and star shaped polymers by free radical polymerization.

Preparation of alkyl methacrylate polymers, random copolymers and block copolymers by anionic polymerization is described in U.S. Patent 4,388,448. Anionic polymerization of alkyl methacrylates affords a synthetic route to block copolymers by sequential addition of monomers. By anionic polymerization, macromolecules can be prepared with predictable molecular weights, controlled stereochemistry and narrow molecular weight distributions.

Anionic polymerization of alkyl methacrylates has not been commercially significant, however, because of two major problems. First, anionic polymerization initiators are inherently reactive with the alkyl methacrylate carbonyl group. This problem has been addressed by the use of bulky initiators, by polymerization at low temperature and by the use of polar solvents.

The second major problem with anionic polymerization of alkyl methacrylates is the inherent presence of chain-terminating protonic contaminants in alkyl methacrylate monomers. Synthesis of alkyl methacrylate monomers involves either esterification or transesterification with the starting alcohol which ultimately defines the ester alkyl. These alcohols may form azeotropes with the alkyl methacrylates and are therefore expensive and difficult to separate from the alkyl methacrylates by distillation. Longer ester alkyl methacrylate monomers are particularly difficult to separate from alcohols because higher distillation temperatures can cause thermal polymerization.

As a consequence of the problems discussed above, most current commercial poly(alkyl methacrylates) are produced utilizing free radical initiators. Free radical polymerization is not sensitive to the presence of the trace amounts of alcohol, but does not realize the advantages of anionic polymerization.

A process to purify alkyl methacrylate monomers has been described by McGrath in R. D. Allen, T. E. Long, S. E. McGrath, *Advances in Polymer Synthesis*, 347-61 (1985), in which monomer was stirred over a drying agent and then subjected to vacuum distillation. Alcohols and remaining protonic contaminants were then titrated with a trialkyl aluminum until a persistent yellow-green complex was formed, and the monomer was then vacuum distilled from the impurities. The yellow-green end point indicates the presence of metal complexes with carbonyls. The trialkylaluminums may react with one, two or three alcohol groups, but will not be available to form complexes while alcohol groups are free due to the great affinity of the metal alkyl for the alcohol group.

A problem inherent with such a use of aluminum alkyls to purify alkyl methacrylates is the possibility that trace oxygen, especially with the presence of UV light, may produce aluminum peroxides, which act as free radical polymerization initiators for alkyl methacrylates. This problem is magnified by the need to distill the monomer from the impurities, and the excess of trialkyl aluminum used.

Purification of higher alkyl methacrylates is particularly troublesome using McGrath's method. Exposure of the monomers to higher temperatures increases the opportunity for initiation of a highly exothermic free radical polymerization. The higher boiling temperatures of longer chain alkyl methacrylates such as 2-ethylhexyl methacrylate and lauryl methacrylate therefore precludes the use of distillation to purify the monomers in the presence of trialkyl aluminums even under reduced pressures.

T. E. Long has suggested the possibility of conducting the polymerizations of alkyl methacrylates in the presence of the resultant aluminum compounds. T. E. Long, PhD Dissertation, Virginia Polytechnic Institute and State University, 211 (October, 1987). This suggestion is not commercially acceptable due to the complexed trialkylaluminum present which is indicated by the yellow-green colour present after addition of trialkyl aluminums according to Long's process.

Long also discloses a second monomer purification technique which avoids the need to distill the monomer from the purification by-products. This method incorporates treating dried monomer with triethyl aluminum, then passing the mixture over a column of alumina which has been prewetted with dry tetrahydrofuran. The alumina absorbs the excess triethyl aluminum and reaction products of alcohol and water and triethyl aluminum. The monomer is then degassed several times. Although this method avoids the need to distill the dried monomer, care must be taken to avoid exotherms as the monomer is passed over the alumina. The column purified monomer anionically polymerized to a homopolymer with a

molecular weight distribution (Mw/Mn) as determined by gel permeation chromatography (GPC) of 1.59. This was an improvement over Long's control example, where polymers were produced from alkyl methacrylates which were purified only by drying with calcium hydrides (2.04) but still falls short of Long's polymers produced from distillation purified monomers (1.35), and remains unsatisfactory for commercial use. An improved process for purifying alkyl methacrylate monomers is therefore still required.

It is therefore an object of the present invention to provide a process to purify alkyl methacrylate monomers for subsequent anionic polymerization which does not require distillation of the monomer in the presence of potential free radical polymerization initiators. It is a further object of the present invention to provide a process to purify alkyl methacrylate monomers to a purified monomer capable of being anionically polymerized to a polymer with a narrow molecular weight distribution.

Accordingly the invention provides a process for preparing a poly(alkyl methacrylate) having a molecular weight distribution between 1.73 and 1.01, comprising:

(i) contacting a starting material comprising an alkyl methacrylate monomer and an alcohol, with an effective amount in the range of from 0.1 to 1.4 mole percent, based on moles of the alkyl methacrylate monomer, of an alcohol-scavenging compound selected from the group consisting of aluminium hydrocarbyl, boron hydrocarbyl, aluminium hydride, boron hydride, and mixtures thereof, under conditions effective for reaction of the alcohol-scavenging compound and the alcohol to produce a mixture comprising the alkyl methacrylate monomer, any remaining alcohol-scavenging compound and reaction by-products; and

(ii) contacting said mixture with an anionic polymerization initiator under anionic polymerization conditions to produce the poly(alkyl methacrylate), wherein the effective amount of alcohol-scavenging compound is less than required for visual detection of the colour of the complex formed between the alcohol-scavenging compound and the alkyl methacrylate monomer.

The process of the present invention permits the preparation of alkyl methacrylate polymers with narrow molecular weight distributions and is particularly advantageous when alkyl methacrylate monomers having alkyl groups containing four or more carbon atoms are to be anionically polymerized. This particular advantage is due to the absence of the need to separate the alcohol-scavenging compound from the monomer prior to polymerization.

In general, alkyl methacrylate monomers useful for the practice of this invention include those capable of anionic polymerization and having the formula $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CO}_2\text{R}$, wherein R can be, for example:

- (a) alkyl of 1 to 18 carbon atoms, branched or unbranched;
- (b) alkenyl of 2 to 18 carbon atoms;
- (c) alkadienyl of 5 to 18 carbon atoms;
- (d) dialkylaminoalkyl of 4 to 12 carbon atoms; or
- (e) alkoxyalkyl of 3 to 12 carbon atoms.

Representative methacrylate monomers include the following:

Alkyl methacrylates such as methyl, ethyl, propyl, butyl, s-butyl, t-butyl, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, and octadecyl methacrylates; alkenyl methacrylates such as vinyl, allyl, methallyl, undecenyl, and 9-octadecenyl methacrylates; alkadienyl methacrylates such as 2,4-pentadienyl, 2,4-hexadienyl, 2,4-octadienyl, 4,7-octadienyl, 9,12-octadecadienyl, and geranyl methacrylates; dialkylaminoalkyl methacrylates such as 2-dimethylaminoethyl, 3-dimethylaminopropyl, 6-diethylaminoethyl, 2-diethylaminoethyl, 2-dibutylaminoethyl, 2-dihexylaminoethyl, and 6-dimethylaminoethyl methacrylates; and alkoxyalkyl methacrylates such as 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, and 3- and 4-methoxybutyl methacrylates.

The choice of the monomer alkyl group affects the properties of the resultant polymer, the ease of hydrolysis to form an acid functionality from the polymer ester groups and, to a large extent, affects the kinetics of polymerization. Each of the potential monomers requires removal of trace alcohols and other protonic contaminants before anionic polymerization may be successfully performed. The most preferred alkyl methacrylates are isobutyl methacrylate and t-butyl methacrylate due to the fact that, with the monomer purification process of the present invention, they may be polymerized at temperatures as high as +25 °C yet retain the desirable attributes of living anionic polymerization.

Water is a protonic contaminate which will terminate chain growth for anionic polymerization. Water must therefore be removed from water-contaminated monomer before anionic polymerization to enable narrow polymer molecular weight distributions and predictable molecular weights.

Water will react with the alcohol scavenging compound of the present invention and, with relatively small quantities of water, the drying step can therefore be eliminated at the expense of the use of more alcohol scavenging compound and increased amounts of by-products in the reaction mixture. Generally, purification of the monomer preferably includes removal of water before contacting the monomer with the

alcohol scavenging compound, because water may be removed from the monomer much easier and more economically than alcohol. Prior removal of water greatly reduces the amount of alcohol-scavenging compound required and greatly reduces the amount of by-products remaining in the monomer which could interfere with polymerization.

Drying is performed by either contact of the monomer with a drying agent such as alumina, silica gel, calcium chloride, or molecular sieves, or by distillation or by a combination of distillation and contact with a drying agent. Distillation of the monomer at this stage of the process is not as undesirable as distillation after contact with the alcohol scavenging agent due to the absence of potential free radical initiators before contact with the alcohol scavenger. Following the drying step, the monomer preferably contains no more than 0.03 weight percent water. Most preferably, the dried monomer contains less than 0.02 percent weight water.

Compounds which are used as alcohol-scavenging compounds in the practice of this invention are aluminum hydrocarbyls, boron hydrocarbyls, aluminum hydrides, boron hydrides and mixtures thereof. The amount of alcohol scavenging compound is within the range of 0.1 mole percent to 1.4 mole percent, based on monomer. Lesser amounts are not sufficient to scavenge alcohols present in commercial grade alkyl methacrylate monomers and greater amounts result in levels of alcohol-scavenging products and excess alcohol scavenger which interfere with anionic polymerization.

According to a preferred embodiment of the present process, as alcohol scavenging compound trialkyl aluminium is used in an amount within the range of from 0.1 to 0.8 mole percent and more preferably in the range of from 0.1 to 0.5 mole percent, based on the moles of the alkyl methacrylate.

According to another preferred embodiment of the present invention, as alcohol scavenging compound alkyl borane is used in an amount of from 0.5 to 1.2 mole percent based on monomer and more preferably in an amount from 0.7 to 0.9 mole percent based on moles of monomer.

An effective amount of alcohol-scavenging compound is from 1/3 to slightly over 1 mole of alcohol-scavenging compound per mole of protonic impurities in the monomer solution. Preferably from 1/2 to 1 mole of alcohol-scavenging compound per mole of protonic impurities is used. At least one mole of the alcohol-scavenging compound per three moles of protonic impurities is required to result in sufficient reaction with the protonic impurities present in the monomer solution. Although a slight excess of alcohol-scavenging agent to protonic impurities does not prevent anionic polymerization of alkyl methacrylate to a narrow molecular weight distribution polymer, sufficient excess to permit visual detection of the colour of the complex formed between the alcohol scavenging agent and the alkyl methacrylate prevents subsequent polymerization of the alkyl methacrylate to a narrow molecular weight range polymer unless the excess was removed from the monomer solution.

Persons skilled in the art will recognize that each species of alcohol-scavenging compound will have a varying optimum dosage and will have a varying range of effective dosages. The upper limit of effectiveness will depend upon the effectiveness of the scavenging compound and the reaction products of the scavenging compound and alcohols as initiators and/or terminators of anionic polymerization. Boron compounds are somewhat less active than aluminum compounds as initiators for undesirable free radical polymerization of alkyl methacrylates and, therefore, may be used in higher dosages without resulting in a polymerized product with unacceptably wide distribution of polymer molecular weights. Higher dosages of boron compounds are also beneficial due to the kinetics of their alcoholysis reaction being generally slower than those of aluminum alkyl compounds.

Hydrocarbyl radicals of the aluminum or boron hydrocarbyls acceptable for the practice of the present invention may be selected from a wide variety of hydrocarbyl groups. The hydrocarbyl may be an alkyl group, a cycloalkyl group, an alkene group or an aromatic group. Any molecular weight group may be used, but preferably the hydrocarbyl group contains from one to 20 carbon atoms. Examples of suitable alkyls include methyl, ethyl, propyl, secondary butyl, tertiary butyl, pentyl, and hexyl. Also acceptable are cycloalkyls containing saturated rings of 5-7 carbon atoms such as cyclopentane, cyclohexane and substituted cyclohexane. Alkene groups of vinyl, allyl, butenyl and pentenyl are acceptable, as are dienyls such as butadienyl and pentadienyl. Mono-unsaturated cyclic hydrocarbon radicals and di-unsaturated cyclic hydrocarbon radicals containing rings with 5-7 carbon atoms are acceptable for the practice of this invention. An example is cyclopentadienyl. Aromatic radicals, substituted aromatics and radicals containing one or more aromatic rings such as naphthyl, tolyl, benzyl and dimethylnaphthyl are acceptable as the hydrocarbyl for the practice of this invention. Because of commercial availability, preferred scavenging agents are aluminum or boron trialkyls wherein the alkyl groups are C₁-4 alkyls. Most preferable are triethyl aluminum and triethyl boron.

The aluminum or boron hydrocarbyl may be contacted with the alkyl methacrylate in a non-protonic solvent, like tetrahydrofuran, ether, hexane, cyclohexane or benzene. The aluminum or boron hydrocarbyl

may also be contacted with the alkyl methacrylate in a solution of essentially the monomer and the aluminum or boron hydrocarbyl.

The time for reaction of the alcohol scavenging compounds with protonic impurities in alkyl methacrylate monomers can vary depending on the reactants and conditions. Contact times as low as 10 seconds could be acceptable, with agitation to aid in the contact and mixing between the alcohol-scavenging compound and any protonic impurities. Preferred contact times are from one minute to two hours and most preferred are from two minutes to one hour. The contact time required would be expected to be inversely related to both the absolute temperature and the amount of agitation provided.

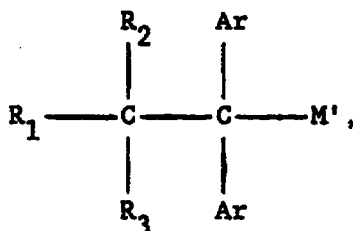
Anionic polymerization of the treated monomer in the practice of this invention can be carried out as known in the art for anionic polymerization of alkyl methacrylates.

Initiators for anionic polymerization of alkyl methacrylates include an organic anion and a counterion of any alkali metal. Lithium is the preferred alkali metal cation.

Representative useful organo(alkali metal) compounds include the following:

1,1-Diphenylhexyl(alkali metals) and preferably 1,1-diphenylhexyl(lithium);

adducts of any alkyl(alkali metal), n-, sec-, or tert-, with any 1,1-diaryl-substituted ethylene provided the aryl substituents are free of electrophilic substituents of the formula



wherein:

R_1 = alkyl,

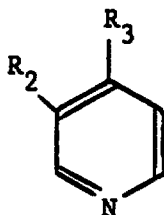
R_2 = H or alkyl,

R_3 = H or alkyl,

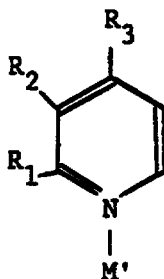
Ar is aryl,

M' = alkali metal and preferably lithium, Diisopropylamido(alkali metals);

an adduct of any secondary or tertiary alkyl(alkali metal)($\text{R}_1\text{M}'$, wherein M' is preferably lithium) with any pyridine unsubstituted in the 2, 5, and 6 positions, i.e.,

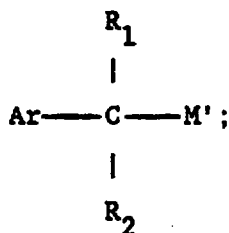


to give the adduct



wherein R_2 and R_3 are non-electrophilic;

cumyl and cumyl-type alkali metal derivatives where substituent limitations are as described above:



and

15 polynuclear hydrocarbon-alkali metal adducts such as naphthalenesodium and biphenylsodium.

Of the foregoing compounds, the diphenylhexyl, cumyl, and diisopropylamido compounds are preferred. The diphenylhexyl compounds can be generated in situ by addition of an organo (alkali metal) compound to 1,1-diphenylethylene.

20 Anionic polymerization of alkyl methacrylates is best carried out in polar solvents that form separated ion-pairs. Breaking down the lithium aggregates imparts a faster initiation rate in addition to retarding intramolecular termination (cyclization). However, pseudo- living conditions may be obtained in non-polar solvents like toluene or hexanes.

25 Tetrahydrofuran (THF) is the preferred solvent. Other ether-type solvents such as 1,2-dimethoxyethane (DME or glyme), diethylene glycol dimethyl ether (diglyme) or mixtures of these with aromatic or saturated hydrocarbons are useful solvents.

The polymerization medium has a direct effect on the polymer tacticity, and hence its glass transition temperature. Non-polar solvents generally result in highly isotactic polymers whereas those produced in polar media are predominantly syndiotactic. This effect is most pronounced for the smaller alkyl esters. For example, poly(methyl) methacrylate may have a difference in T_g of 80°C between syndiotactic and isotactic microstructures, whereas, poly(tertiary-butyl) methacrylate (PTBMA) has a corresponding T_g differential of only 20°C .

35 A typical total monomer charge is one mole in one liter of solvent (1 M) and initiator concentrations are typically between 0.1 M and 0.0015 M. At this molarity, the solutions are 10 to 15% solids when polymerization is complete. Lower concentrations (5 to 10%) are acceptable. Higher concentrations (above 15%) cause increased viscosity which may interfere with proper mixing during the latter stages of monomer addition. Incomplete mixing may lead to an undesirable broadening in molecular weight distribution. The rate of monomer addition should be maintained so as to keep the reaction temperature within an acceptable temperature range.

40 The temperature required for polymerization of alkyl methacrylates to polymers having narrow molecular weight distributions varies with the particular alkyl methacrylate monomer being polymerized. With monomers treated according to this invention, it has been observed that tertiary butyl methacrylate can be polymerized at as high as 25°C . Isobutyl methacrylate may be polymerized at a temperature as high as 0°C . Polymerization of methyl methacrylate must be performed below -40°C to result in a polymer having narrow molecular weight distribution. It is important that the temperature of the polymerization be at or below the particular required temperature.

45 The polymerization can be terminated with a protic material such as water, methanol or acetic acid, and the polymer can be isolated by stripping off the solvent. Alternatively, the polymer can be precipitated in an appropriate non solvent such as water or alcohol.

50 Poly(alkyl methacrylates) produced by the process of this invention have molecular weight distribution (M_w/M_n) of between 1.73 and 1.01 and preferably between 1.01 and 1.10.

Examples

55 In Examples 1 through 14, tertiary butyl methacrylate was purified by the process of the present invention and subsequently polymerized at 25°C using diphenylhexyl lithium as an initiator. Example 15 is a comparison example, with no alcohol scavenger used. Triethyl aluminium was utilized as the alcohol scavenger in amounts of 1.4, 1.3, 1.0, 0.8, 0.5, 0.2 and 0.1 mole % based on the moles of the monomer for Examples 1, 3, 5, 7, 9, 11 and 13, respectively. Triethyl boron was utilized as the alcohol scavenger at

levels of 1.4, 1.3, 1.0, 0.8, 0.5, 0.2, and 0.1 mole % based on the moles of the monomer for Examples 2, 4, 6, 8, 10, 12 and 14, respectively.

Table 1 is a summary of Examples 1-15 alcohol scavenger type, amount, molecular weight distribution of polymer, theoretical molecular weight (grams monomer/moles initiator) and molecular weight as measured by GPC with polystyrene standards.

Tertiary butyl methacrylate (TBMA) was dried by stirring over calcium hydride for approximately twelve hours, then vacuum distilled. After the drying, the monomer contained 0.1 to 0.3 mole percent alcoholic impurities as determined by gas chromatography.

The dried TBMA was then combined with the alcohol scavenging agent and stirred for approximately 30 minutes at approximately room temperature. Both triethyl aluminium and triethyl boron were purchased and used as a 1.0 molar solution in tetrahydrofuran (THF).

For each Example 1-15, a purged polymerization bottle equipped with a stir bar and a heavy duty rubber septum was charged with 210 ml of anhydrous THF and a two-fold excess of 1,1-diphenylethylene (DPE) based on moles s-BuLi. After equilibration to a temperature of about 25 °C the THF/DPE solution was titrated to remove protic impurities by adding s-BuLi until a faint, persistent pink colour of diphenylhexyllithium was observed. Additional THF was added dropwise until the pink colour disappeared. At this point the charge of s-BuLi necessary to polymerize the monomer to a targeted molecular weight was added. This resulted in a dark red solution of diphenylhexyllithium. The methacrylate monomer, treated with either TEA, TEB or untreated was added dropwise into the reactor via a double ended needle. The red colour disappeared upon addition of the first drops of monomer which is indicative of the colourless polyenolate. The polymerization was allowed to proceed for 20 minutes before termination with MeOH. The polymers were stabilized with Irganox 1010 antioxidant, isolated by precipitation in MeOH, and dried to a constant weight in a vacuum oven.

TABLE 1

Example No.	MR ₃	(MR ₃) Mole %	M _w /M _n	Mn(theory)	Mn(GPC)
1	TEA	1.4	1.73	25.10 M	34.11 M
2	TEB	1.4	1.28	24.90 M	26.71 M
3	TEA	1.3	1.71	25.92 M	33.08 M
4	TEB	1.3	1.20	27.93 M	28.33 M
5	TEA	1.0	1.36	24.20 M	23.57 M
6	TEB	1.0	1.16	21.96 M	22.62 M
7	TEA	0.8	1.28	22.85 M	25.30 M
8	TEB	0.8	1.08	26.86 M	26.80 M
9	TEA	0.5	1.26	25.05 M	25.82 M
10	TEB	0.5	1.16	23.85 M	24.41 M
11	TEA	0.2	1.06	36.12 M	37.57 M
12	TEB	0.2	1.14	25.80 M	26.02 M
13	TEA	0.1	1.10	25.80 M	25.97 M
14	TEB	0.1	1.43	31.00 M	34.60 M
15*	-	0	2.00	24.65 M	19.77 M

* Example 15 is a comparison example.

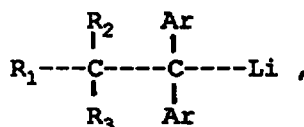
Example 16 was an attempt to purify tertiary butyl methacrylate using the prior art process of titrating the monomer with triethyl aluminium until a yellow-green endpoint is reached, then vacuum distillation of the monomer from the reaction products of the triethyl aluminium and alcohol and the excess triethyl aluminium.

In Example 16, tertiary butyl methacrylate monomer was stirred over CaH₂ under a nitrogen pressure for over 24 hours. The monomer was then vacuum distilled from the CaH₂, yielding 22.5 ml of dry monomer. Triethyl aluminium was added until the solution was a yellow-green colour. The monomer polymerized within 30 minutes of the addition of the triethyl aluminium by free radical polymerization, forming a useless gel and preventing anionic polymerization.



Claims

1. A process for preparing a poly(alkyl methacrylate) having a molecular weight distribution between 1.73 and 1.01 comprising:
 - (i) contacting a starting material comprising an alkyl methacrylate monomer and an alcohol, with an effective amount in the range of from 0.1 to 1.4 mole percent, based on moles of the alkyl methacrylate monomer, of an alcohol-scavenging compound selected from the group consisting of aluminium hydrocarbyl, boron hydrocarbyl, aluminium hydride, boron hydride, and mixtures thereof, under conditions effective for reaction of the alcohol-scavenging compound and the alcohol to produce a mixture comprising the alkyl methacrylate monomer, any remaining alcohol-scavenging compound and reaction by-products; and
 - (ii) contacting said mixture with an anionic polymerization initiator under anionic polymerization conditions to produce the poly(alkyl methacrylate), wherein the effective amount of alcohol-scavenging compound is less than required for visual detection of the colour of the complex formed between the alcohol-scavenging compound and the alkyl methacrylate monomer.
2. The process of claim 1 wherein the alcohol scavenging agent is aluminium alkyl present in an amount within the range of 0.1 to 0.8 mole percent, based on moles of the alkyl methacrylate monomer.
3. The process of claim 2 wherein the aluminium alkyl is present in an amount within the range of from 0.1 to 0.5 mole percent, based on the moles of the alkyl methacrylate monomer.
4. The process of claim 1 wherein the alcohol scavenging compound is an alkyl borane.
5. The process of claim 4 wherein the amount of alcohol scavenging agent is from 0.5 to 1.2 mole percent based on monomer.
6. The process of claim 5 wherein the amount of alcohol scavenging agent is from 0.7 to 0.9 mole percent based on moles of monomer present.
7. The process of claim 1 wherein the alcohol scavenging agent is triethyl borane.
8. The process of claim 1 wherein the alcohol scavenging agent is triethyl aluminium.
9. The process of claim 1 wherein the alkyl methacrylate is selected from the group consisting of branched or unbranched C₁-C₁₈ alkyl methacrylates, C₂-C₁₈ alkenyl methacrylates, C₅-C₁₈ alkadienyl methacrylates, C₄-C₁₂ dialkylaminoalkyl methacrylates, and C₃-C₁₂ alkoxyalkyl methacrylates.
10. The process of claim 9 wherein the alkyl methacrylate is selected from the group consisting of branched or unbranched C₁-C₁₈ alkyl methacrylates.
11. The process of claim 1 wherein the alkyl methacrylate is selected from the group consisting of isobutyl methacrylate and tertiary butyl methacrylate.
12. The process of claim 1 wherein as initiators for the anionic polymerization, lithium compounds selected from the group consisting of 1,1-diphenylhexyl(lithium); adducts of any alkyl lithium, n-, sec-, tert-, with any 1,1-diaryl-substituted ethylene provided the aryl substituents are free of electrophilic substituents of the formula



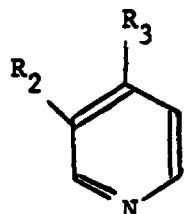
wherein

R₁ = alkyl,

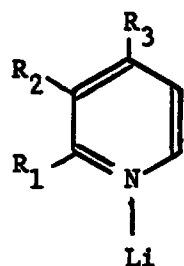
R₂ = H or alkyl,



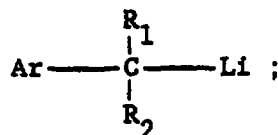
R_3 = H or alkyl, and
 Ar = aryl;
 diisopropylamido lithium;
 an adduct of any secondary or tertiary alkyl lithium (R_1Li) with any pyridine unsubstituted in the 2,5
 and 6 positions, i.e.



to give the adduct



wherein R_2 and R_3 are non-electrophilic;
 cumyl and cumyl-type lithium compounds wherein substituent limitations are as described herein-
 before:



and polynuclear hydrocarbon-alkali metal adducts such as naphthalene-sodium and biphenylsodium are used.

13. Process of claim 12, wherein as initiators diphenylhexyl-, cumyl-, and diisopropylamido-lithium compounds are used.

14. The process of claim 1 wherein the poly(alkyl methacrylate) produced has a molecular weight distribution within the range of 1.01 to 1.10.

Patentansprüche

1. Verfahren zur Herstellung eines Polyalkylmethacrylats mit einer Molekulargewichtsverteilung zwischen 1,73 und 1,01, bei dem man:

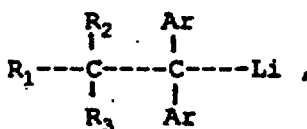
(i) ein Ausgangsprodukt aus einem Alkylmethacrylat-Monomer und einem Alkohol mit einer wirkungsvollen, im Bereich von 0,1 bis 1,4 Mol-%, bezogen auf Mol Alkylmethacrylat-Monomer, liegenden Menge einer alkoholbindenden Verbindung, ausgewählt aus der Gruppe Aluminiumhydrocarbyl, Borhydrocarbyl, Aluminiumhydrid, Borhydrid und deren Mischungen, unter zur Umsetzung der alkoholbindenden Verbindung mit dem Alkohol zu einer Mischung aus Alkylmethacrylat-Monomer, eventuell noch vorhandener alkoholbindender Verbindung und Reaktionsnebenprodukte wir-



kungsvollen Bedingungen kontaktiert, und

(ii) diese Mischung unter anionischen Polymerisationsbedingungen mit einem anionischen Polymerisationsstarter kontaktiert und auf diese Weise das Polyalkylmethacrylat herstellt, wobei die wirksame Menge der alkoholbindenden Verbindung geringer ist als zum visuellen Nachweis der Farbe des von der alkoholbindenden Verbindung und dem Alkylmethacrylat-Monomer gebildeten Komplexes erforderlich ist.

2. Verfahren nach Anspruch 1, wobei das alkoholbindende Mittel Aluminiumalkyl ist und in einer Menge im Bereich von 0,1 bis 0,8 Mol-%, bezogen auf Mol Alkylmethacrylat-Monomer, vorliegt.
3. Verfahren nach Anspruch 2, wobei das Aluminiumalkyl in einer Menge im Bereich von 0,1 bis 0,5 Mol-%, bezogen auf Mol Alkylmethacrylat-Monomer, vorliegt.
4. Verfahren nach Anspruch 1, wobei die alkoholbindende Verbindung ein Alkylboran ist.
5. Verfahren nach Anspruch 4, wobei die Menge an alkoholbindender Verbindung 0,5 bis 1,2 Mol-%, bezogen auf das Monomer, beträgt.
6. Verfahren nach Anspruch 5, wobei die Menge an alkoholbindender Verbindung 0,7 bis 0,9 Mol-%, bezogen auf Mol vorhandenem Monomer, beträgt.
7. Verfahren nach Anspruch 1, wobei die alkoholbindende Verbindung Triethylboran ist.
8. Verfahren nach Anspruch 1, wobei die alkoholbindende Verbindung Aluminiumtriethyl ist.
9. Verfahren nach Anspruch 1, wobei das Alkylmethacrylat aus der Gruppe verzweigter oder unverzweigter C₁-C₁₈-Alkylmethacrylate, C₂-C₁₈-Alkenylmethacrylate, C₅-C₁₈-Alkadienylmethacrylate, C₄-C₁₂ Dialkylaminoalkylmethacrylate und C₃-C₁₂-Alkoxalkylmethacrylate ausgewählt ist.
10. Verfahren nach Anspruch 9, wobei das Alkylmethacrylat aus der Gruppe verzweigter oder unverzweigter C₁-C₁₈-Alkylmethacrylate ausgewählt ist.
11. Verfahren nach Anspruch 1, wobei das Alkylmethacrylat aus der Gruppe Isobutylmethacrylat und tertiärem Butylmethacrylat ausgewählt ist.
12. Verfahren nach Anspruch 1, wobei als Starter für die anionische Polymerisation Lithiumverbindungen, die ausgewählt sind aus der Gruppe 1,1-Diphenylhexyllithium, Anlagerungsprodukte eines beliebigen -n-, -sec- oder -tert-alkyllithiums an ein beliebiges 1,1-diarylsubstituiertes Ethylen, vorausgesetzt, die Arylsubstituenten sind frei von elektrophilen Substituenten, der Formel:



worin:

R₁ = Alkyl,

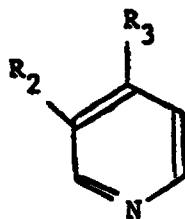
R₂ = H oder Alkyl,

R₃ = H oder Alkyl und

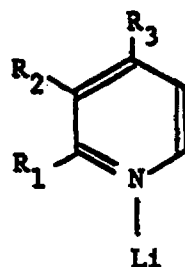
Ar = Aryl bedeuten,

Lithium-diisopropylamide,

das Anlagerungsprodukt eines beliebigen sekundären oder tertiären Alkylolithiums (R₁Li) an ein beliebiges Pyridin, das in der 2-, 5- und 6-Stellung unsubstituiert ist, also

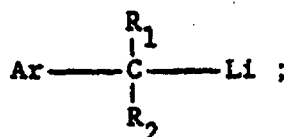


10 unter Bildung des Anlagerungsprodukts



worin R_2 und R_3 nichtelektrophil sind,

25 Cumyl- und Lithiumverbindungen des Cumyltyps, worin die Substituenten die oben beschriebene eingeschränkte Bedeutung besitzen:



35 sowie mehrkernige Anlagerungsverbindungen aus Kohlenwasserstoff und Alkalimetall wie Naphthalinnatrium und Biphenylnatrium eingesetzt werden.

13. Verfahren nach Anspruch 12, wobei als Starter Diphenylhexyllithium-, Cumyllithium- und Lithiumdiisopropylamidverbindungen eingesetzt werden.
- 40 14. Verfahren nach Anspruch 1, wobei das hergestellte Polyalkylmethacrylat eine Molekulargewichtsverteilung im Bereich von 1,01 bis 1,10 besitzt.

Revendications

- 45 1. Un procédé pour la préparation d'un poly(méthacrylate d'alcoyle) ayant une distribution des poids moléculaires comprise entre 1,73 et 1,01, comprenant :

(1) la mise en contact d'une matière de départ comprenant un monomère méthacrylate d'alcoyle et un alcool avec une quantité efficace comprise entre 0,1 et 1,4 mole pour cent, par rapport aux moles du monomère méthacrylate d'alcoyle, d'un composé fixant les alcools choisi dans le groupe constitué par les aluminium-hydrocarbyles, les bore-hydrocarbyles, les hydrures d'aluminium, les hydrures de bore et leurs mélanges, dans des conditions convenables pour réaction du composé fixant les alcools et de l'alcool afin de produire un mélange comprenant le monomère méthacrylate d'alcoyle, tout reste du composé fixant les alcools et des sous-produits de réaction ; et

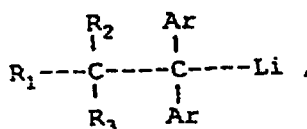
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(2) la mise en contact de ce mélange avec un initiateur de polymérisation anionique dans des conditions de polymérisation anionique afin de produire le poly(méthacrylate d'alcoyle), où la quantité efficace de composé fixant les alcools est inférieure à celle nécessaire pour détection visuelle de la couleur du complexe formé entre le composé fixant les alcools et le monomère méthacrylate d'alcoyle.

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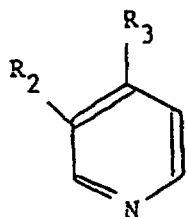


2. Le procédé selon la revendication 1 dans lequel l'agent fixant les alcools est un aluminium-alcoyle présent dans une quantité comprise dans l'intervalle de 0,1 à 0,8 mole pour cent, par rapport aux moles du monomère méthacrylate d'alcoyle.
- 5 3. Le procédé selon la revendication 2 dans lequel l'aluminium-alcoyle est présent dans une quantité comprise dans l'intervalle de 0,1 à 0,5 mole pour cent, par rapport aux moles du monomère méthacrylate d'alcoyle.
4. Le procédé selon la revendication 1 dans lequel le composé fixant les alcools est un alcoylborane.
- 10 5. Le procédé selon la revendication 4 dans lequel la quantité de l'agent fixant les alcools est comprise entre 0,5 et 1,2 mole pour cent par rapport au monomère.
6. Le procédé selon la revendication 5 dans lequel la quantité de l'agent fixant les alcools est comprise
- 15 entre 0,7 et 0,9 mole pour cent par rapport aux moles de monomère présentes.
7. Le procédé selon la revendication 1 dans lequel l'agent fixant les alcools est le triéthylborane.
8. Le procédé selon la revendication 1 dans lequel l'agent fixant les alcools est le triéthylaluminium.
- 20 9. Le procédé selon la revendication 1 dans lequel le méthacrylate d'alcoyle est choisi dans le groupe constitué par les méthacrylates d'alcoyle en C₁-C₁₈ ramifiés ou non, les méthacrylates d'alcényle en C₂-C₁₈, les méthacrylates d'alcadiényle en C₅-C₁₈, les méthacrylates de dialcoylaminoalcoyle en C₄-C₁₂ et les méthacrylates d'alcoxyalcoyle en C₃-C₁₂.
- 25 10. Le procédé selon la revendication 9 dans lequel le méthacrylate d'alcoyle est choisi dans le groupe constitué par les méthacrylates d'alcoyle en C₁-C₁₈ ramifiés ou non.
11. Le procédé selon la revendication 1 dans lequel le méthacrylate d'alcoyle est choisi dans le groupe
- 30 constitué par le méthacrylate d'isobutyle et le méthacrylate de butyle tertiaire.
12. Le procédé selon la revendication 1 dans lequel, comme initiateurs pour la polymérisation anionique, on utilise des composés du lithium choisis dans le groupe constitué par le 1,1-diphénylhexyllithium ; des adducts de n'importe quel alcoyllithium, n-, sec- ou tert-, avec n'importe quel 1,1-diaryl éthylène du
- 35 moment que les substituants aryle sont exempts de substituants électrophiles, de la formule

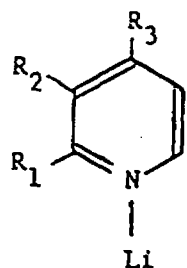


dans laquelle :

- 45 R₁ est un groupe alcoyle,
- R₂ est H ou un groupe alcoyle,
- R₃ est H ou un groupe alcoyle et
- Ar est un groupe aryle ;
- le diisopropylamido lithium ;
- un adduct de n'importe quel lithium-alcoyle secondaire ou tertiaire (R₁Li) avec n'importe quelle
- 50 pyridine non-substituée dans les positions 2, 5 et 6, c'est-à-dire

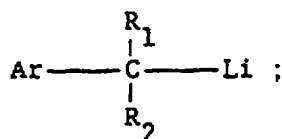


pour donner l'adduct



où R_2 et R_3 sont non-électrophiles ;

des composés cumyllithium et du même type où les limitations concernant les substituants sont telles que décrites ci-dessus ;



et des adducts hydrocarbure polycyclique-métal alcalin tels que naphthalène-sodium et biphenylsodium.

13. Procédé selon la revendication 12, dans lequel, on utilise comme initiateurs des composés diphenylhexyl-, cumyl- et diisopropylamido-lithium.

14. Le procédé selon la revendication 1 dans lequel le poly(méthacrylate d'alcoyle) produit a une distribution des poids moléculaires comprise dans l'intervalle de 1,01 à 1,10.