

## **Method for producing a multi-phase polymer system**

The present invention relates to the technical field of polymerisation methods, which are used in a wide variety of forms, both in terms of the apparatus employed and the method conditions, for the targeted production of plastics with specific property profiles. More specifically, the invention proposes a method for producing a multi-phase polymer system comprising at least a two-stage RAFT polymerisation, the steps of which are each carried out in the presence of a specific RAFT controller substance. The most important application background for the multi-phase polymer systems produced in this way is pressure-sensitive adhesives for adhesive tapes, which are used in various technical fields to create both temporary and permanent material bonds.

For industrial adhesive tape applications, polymers based on the polymerisation of monomers with functionalised vinyl groups are frequently used. A well-known example of such polymers are poly(meth)acrylates. Poly(meth)acrylates offer various advantages over other plastics used as a basis for adhesive applications. For example, they are highly resistant to high-energy radiation and oxidising substances. In contrast to poly(meth)acrylates, synthetic rubbers and natural rubbers often contain C-C double bonds, which make these polymers - and consequently the adhesive components based on them - vulnerable to, for example, UV radiation, oxygen and ozone. Furthermore, poly(meth)acrylate-based plastic formulations can be transparent and are suitable for use across a wide temperature range.

An important factor that influences the properties of polymers based on monomers with functionalised vinyl groups is the polymer architecture. In the distant past, work was mostly carried out with random copolymers, in which the monomers are randomly distributed along the polymer chain. In recent decades, the focus has shifted to polymers with controlled structures, such as block copolymers or copolymers with a monomer distribution gradient. The aim is therefore to specifically control the property profile of the polymers and the resulting plastic formulations via the distribution or arrangement of the monomers. In this way, it is possible to achieve properties that are inherently contradictory using one and the same polymer base. In this context, so-called RAFT polymerisation has proven to be a highly suitable method.

‘RAFT polymerisation’ stands for ‘reversible addition-fragmentation chain transfer polymerisation’. This refers to a polymerisation in which the reaction is controlled by reversible chain transfer reactions. In this process, an active, growing radical chain adds to a specific

controller substance, the so-called RAFT agent, which is already linked to another chain and is thus present as a higher-molecular-weight RAFT agent (macro-RAFT agent). The addition of the active radical chain produces an intermediate which, due to its structure, has the potential to fragment in various directions. This process again yields a macro-RAFT agent and an active radical chain available for propagation, wherein the latter need not correspond to the previous active radical chain. In this way, the probability of propagation is distributed equally across all chains, resulting in a tight molecular weight distribution.

Methods for the controlled polymerisation of (meth)acrylates are described in the prior art.

WO 2004/101627 A1 describes a method for the continuous polymerisation of acrylic monomers to polyacrylates in the presence of polymerisation-controller substances, wherein at least one polymerisation step is carried out within at least one reaction extruder.

WO 2013/072120 A1 relates to a method for producing acrylate-based polymers, in which a controlled radical polymerisation reaction of a reaction mixture comprising at least one acrylate-based monomer is first carried out in the presence of at least one controller substance having at least one functional group  $S-C=X$ , where  $X = S, O$  or  $N$ , wherein the controller substance is selected from the group comprising dithioesters, dithiocarbonates, dithiocarbamates, trithiocarbonates, imido-dithio-carbonates and xanthates ('RAFT controllers'),

wherein the majority of the controller substance molecules are incorporated into the resulting polymer chains, whereupon the respective polymer chain exhibits the functional group of the incorporated controller,

characterised in that

at least one chemical compound having at least two conjugated double bonds (hereinafter referred to as a "conjugated diene") is brought into contact with the polymers thus obtained,

so that hetero-Diels-Alder reactions are induced between the  $C=X$  double bonds of the functional groups  $S-C=X$  incorporated into the polymer chains and the conjugated double bonds of the conjugated diene.

EP 2 607 394 A1 discloses a method for producing pressure-sensitive adhesives, in which a controlled radical polymerisation reaction of a reaction mixture comprising one or more monomers is carried out in the presence of at least one radical initiator to produce at least one polymer, characterised in that

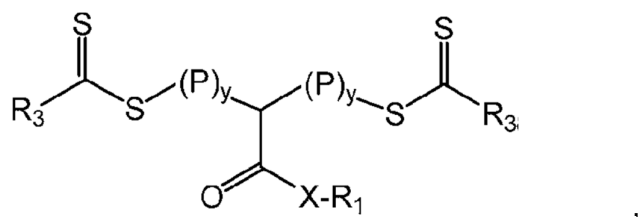
at least one cyclic 1,4-diradical is used as the radical initiator, which is generated by means of a cyclisation reaction from a compound having at least two unsaturated C-C bonds ("diradical-forming compound"),

wherein the polymerisation reaction is carried out in the presence of at least one controller substance ("polymerisation controller").

WO 2013/055978 A1 describes acrylic copolymers which involve the controlled placement of specific functional groups within the polymer structure. The copolymers contain at least two reactive segments and are produced via a controlled radical polymerisation method. The copolymers are suitable for use in the production of adhesives and elastomers.

WO 2018/118905 A1 describes a cross-linkable composition comprising

a) a polymeric material of the formula



wherein

R<sub>1</sub> is hydrogen, alkyl, fluorinated alkyl, aryl, aralkyl or substituted aralkyl;

X is oxygen or -NR<sub>2</sub>, wherein R<sub>2</sub> is hydrogen, alkyl, fluorinated alkyl, aryl, aralkyl or substituted aryl;

each R<sub>3</sub> is an alkoxy, fluorinated alkoxy or -N(R<sub>4</sub>)<sub>2</sub>, wherein each R<sub>4</sub> is alkyl or fluorinated alkyl or, together with the nitrogen to which they are both attached, forms a heterocyclic ring;

each P is a polymeric block comprising a polymerised product of a first monomer composition comprising at least one monomer having a single ethylenically unsaturated group;

- y is an integer from 1 to 5; and
- b) a second monomer composition which is miscible with the polymeric material of the formula and comprises a cross-linking monomer having at least two ethylenically unsaturated groups.

WO 2018/178829 A1 describes controlled radical initiators, reaction mixtures containing these and various ethylenically unsaturated monomers; polymeric materials formed from these reaction mixtures; cross-linkable compositions containing the polymeric materials; and cross-linked compositions formed therefrom. The controlled radical initiators are bis-dithiocarbamate and bis-dithiocarbonate compounds having a single carbon atom between the two dithiocarbamate or dithiocarbonate groups.

Polymers based on monomers with functionalised vinyl groups were previously routinely produced from solution and, naturally, further processed in this form, for example into (adhesive) bonding compounds. The polymerisates, which may be blended with other substances, are coated onto a substrate from solution using a coating bar or a similar tool and then dried. To increase cohesion, the polymers are usually cross-linked, which is typically achieved either thermally, by UV radiation or by electron beam irradiation. The solvent process is, on the whole, economically rather inefficient and environmentally harmful, as the solvents are either not recovered and thus pollute the environment, or must be recovered at high energy cost.

Furthermore, quality issues regularly arise. For instance, adhesive tapes with a higher coating weight based on the polymers described can often scarcely be produced without bubbles.

To mitigate these drawbacks, attempts have been made to apply the polymers - or the compounds produced from them - from the melt to the substrate in a so-called hot-melt process during the manufacture of adhesive tapes. However, this technique also has its limitations. It is inherent in the nature of a hot-melt process that the polymers are exposed to high temperatures during processing from the melt. If, in RAFT polymerisation for the production of the polymers, certain RAFT controller substances such as symmetrically substituted trithiocarbonates are used, the resulting polymers contain a central trithiocarbonate group. This group is thermally unstable and can therefore decompose during the hot-melt process. Such

decomposition processes manifest themselves in polymer degradation and, consequently, in the case of, for example, adhesive compounds, in a measurable loss of cohesion.

WO 98/01478 A1 relates to a free-radical polymerisation process comprising bringing into contact:

- (i) a monomer selected from the group consisting of vinyl monomers, maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerisable monomers;
- (ii) a thiocarbonylthio compound having a chain transfer constant greater than 0.1; and
- (iii) free radicals from a suitable source

as well as adjusting the polydispersity of the polymer by varying the ratio of the number of molecules (ii) to the number of molecules (iii).

In this context, thiocarbonylthio compounds are proposed which lead to polymers that are subject to degradation under thermal stress and thus to a loss of cohesion.

EP 1 312 658 A2 describes pressure-sensitive adhesive systems comprising at least one pressure-sensitive adhesive composition based on at least one block copolymer,

wherein the weight proportions of the block copolymers together account for at least 50% of the pressure-sensitive adhesive composition,

wherein at least one block copolymer is composed at least partly on the basis of (meth)acrylic acid derivatives,

wherein, furthermore, at least one block copolymer comprises at least the unit P(A)-P(B)-P(A) consisting of at least one polymer block P(B) and at least two polymer blocks P(A), and wherein

- P(A) independently represents homo- or copolymer blocks of monomers A, wherein the polymer blocks P(A) each have a softening temperature in the range from +20°C to +175°C,
- P(B) represents a homopolymer or copolymer block of monomers B, wherein the polymer block P(B) has a softening temperature in the range from -130°C to +10°C,
- the polymer blocks P(A) and P(B) are not homogeneously miscible with one another,

characterised in that

the pressure-sensitive adhesive system is oriented in that it has a preferred direction, wherein the refractive index  $n_{MD}$  measured in the preferred direction is greater than the refractive index  $n_{cd}$  measured in a direction perpendicular to the preferred direction. The pressure-sensitive adhesive compositions are applied from the melt. This document also describes controller substances that appear to be critical with regard to polymer degradation due to thermal stress.

One object of the invention was to avoid the problems known from the prior art and to provide a method for producing polymers on the basis of monomers with functionalised vinyl groups, by means of which polymers with a controlled architecture and tight molecular weight distribution can be produced in such a way that in the event of subsequent thermal load, their mechanical properties are largely maintained.

A further object of the invention was to provide such a method that offers a high degree of flexibility for changes to the polymer formulation and the desired polymer architecture.

A supplementary object of the invention was to provide polymers producible in this manner with good cohesion and good processability from the melt.

In particular, an object of the invention was to provide polymers based on monomers with functionalised vinyl groups, having a controlled architecture and tight molecular weight distribution, which can withstand coating onto a substrate from the melt without significant loss of cohesion.

A further supplementary objective of the invention was to provide such polymers that are particularly well suited for adhesive tape applications.

A first and general subject of the invention, by which these objects are achieved, is a method for producing a polymer system available in at least two phases, comprising the steps:

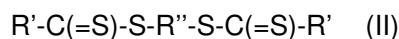
- a) RAFT polymerisation of a monomer composition I, comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, in order to form a polymerisate A; and
- b) RAFT polymerisation of a monomer composition II, comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, wherein at least 50 wt.% of the monomers in monomer

composition II differ from those in monomer composition I, in the presence of polymerisate A in order to form polymerisate B, thereby obtaining a polymer system which is available in at least two phases and comprises polymerisates A and B;

characterised in that the RAFT polymerisations of steps a) and b) are carried out independently of one another in the presence of a RAFT controller substance which, in its original state, corresponds to the general structure (I)



the general structure (II)



wherein

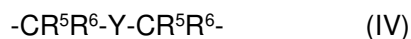
the substituents  $R'$  independently of one another represent an aryl, aralkyl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio, alkoxy, alkaryloxy or alkenoxy group or a group  $(NR^1)_2$ , wherein the substituents  $R^1$  independently of one another represent an alkyl or aryl group or, together with the N atom, form a heterocyclic ring containing 1 to 3 heteroatoms, independently selected from the group consisting of N, O and S;

R represents a sec- or tert-alkyl group, a cyano-sec-alkyl group, a cyano-tert-alkyl group, a carboxy-tert-alkyl group, a carboxy-sec-alkyl group, an aralkyl group or a group of the general structure (III)



wherein  $R^2$  represents an alkyl group or H,  $R^3$  represents a cyano, carboxy or carboxylic acid ester group, and  $R^4$  represents an aryl group; and

$R''$  represents a group of the general structure (IV)



wherein  $R^5$  and  $R^6$  independently represent a hydrogen atom, an n-alkyl group, a cyano group, a carboxy group or a carboxylic acid ester group, and

Y represents an alkylene or arylene group, or a group having a structure selected from  $-(CH_2)_m-CO-O-(CH_2)_n-O-CO-(CH_2)_m-$  and  $-(CH_2)_m-CO-NR^7-(CH_2)_n-NR^7-CO-(CH_2)_m-$ , wherein n represents an integer from 1 to 12; m represents 0 to 4; and  $R^7$  represents an organyl group.

It has been shown that multi-phase polymer systems can be produced in this way from solution, which survive even the subsequent removal of the solvent - which is regularly associated with particularly high temperatures - without significant loss of cohesion and can subsequently be further processed from the melt largely without difficulty.

Details and embodiments of the invention are described below. Such embodiments which are hereinafter designated in any form as preferred are combined in particularly preferred embodiments with features of other embodiments designated in any form as preferred. Combinations of two or more of the embodiments described below as 'particularly preferred' in any form are therefore particularly preferred. Also preferred are embodiments in which a feature of an embodiment described as 'preferred' to any extent is combined with one or more further features of other embodiments described as 'preferred' to any extent.

Insofar as both specific quantities or proportions of an element and preferred embodiments of the element are disclosed below, the specific quantities or proportions of the preferred embodiments are also disclosed in particular. Furthermore, it is disclosed that, for the corresponding specific total quantities or total proportions of the elements, at least some of the elements may be in a preferred configuration and, in particular, that elements in a preferred configuration may in turn be present within the specific total quantities or total proportions.

The term 'polymer system' as used in the invention refers to both a single polymer and a mixture of two or more different polymers. In accordance with the understanding of those skilled in the art, a "polymer" or "a single polymer" is understood to mean not only a single macromolecule, but also a plurality of macromolecules originating from one and the same polymerisation process and exhibiting a specific molecular weight distribution amongst themselves.

The polymer system resulting from the method according to the invention exists in at least two phases. The person skilled in the art understands this to mean that one phase is rich in one component of the polymer system, for example polymerisate A, or consists substantially of that component, and the other phase is rich in another component, for example polymerisate B, or consists substantially of that component. The presence of small amounts of one component in the other, which does not prevent the formation of the multi-phase system, is regarded as

negligible. If the polymer system resulting from the method according to the invention comprises more than two phases, the foregoing applies accordingly to all of these phases.

The phase separation is particularly preferably carried out in such a way that discrete regions ('domains'), which are rich in polymerisate A or polymerisate B – i.e. are substantially formed from polymerisate A or polymerisate B – are present in a continuous matrix which is rich in the respective other polymer – i.e. is substantially formed from the respective other polymerisate.

A polymer system resulting from the method according to the invention is regarded as being available in at least two phases in particular if at least one of the criteria a) – c) listed below is met:

- a) Phase boundaries are discernible in an elevation profile analysis of an *atomic force* microscopy (AFM) image of the polymer system.
- b) At least two independent glass transition temperatures are obtained from a differential scanning calorimetry (DSC) measurement performed on the polymer system.
- c) At least two  $\tan \delta$  maxima are obtained from a dynamic mechanical analysis (DMA) performed on the polymer system.

According to the invention, the polymer system, which is available in at least two phases, also comprises a microphase-separated polymer system, i.e. a polymer system in which the discontinuous phase is present in a microscopically fine distribution.

The method according to the invention comprises a step a) in which the RAFT polymerisation of a monomer composition I, comprising in total at least 80 wt.%, based on the total weight of the monomer composition I, of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers having at least one polymerisable vinyl group, to form a polymerisate A.

Preferably, the monomer composition I comprises one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers having at least one polymerisable vinyl group in an amount of at least 85 wt.%, more preferably at least 90 wt.%, particularly preferably at least 95 wt.%, and in particular at least 98 wt.%. Most particularly preferably, the monomer composition I comprises exclusively one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers having at least one polymerisable vinyl group.

The RAFT polymerisation of step a) may in principle be carried out in any manner. Preferably, it is carried out in a solvent, in particular in a solvent in a conventional reactor designed for such polymerisations.

The polymerisate A resulting from the polymerisation of step a) is preferably a polymer block from which, or to which, at least one further, distinguishable polymer block can be polymerised.

The method according to the invention comprises a step b) in which, in the presence of polymerisate A, the RAFT polymerisation of a monomer composition II is carried out, which comprises, in total, at least 80 wt.%, based on the total weight of monomer composition I, of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers having at least one polymerisable vinyl group, wherein at least 50 wt.% of the monomers in monomer composition II differ from those in monomer composition I, to form a polymerisate B, yielding a polymer system available in at least two phases comprising polymerisates A and B.

Preferably, the monomer composition II comprises one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers having at least one polymerisable vinyl group in an amount of at least 85 wt.%, more preferably at least 90 wt.%, particularly preferably at least 95 wt.%, and in particular at least 98 wt.%. Most particularly preferably, monomer composition II comprises exclusively one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers having at least one polymerisable vinyl group.

The RAFT polymerisation of step b) may also, in principle, be carried out in any manner. Preferably, it is carried out in a solvent, in particular in a solvent in a conventional reactor designed for such polymerisations.

In step a), radical formation and thus polymerisation is preferably initiated by radiation, particularly preferably by UV radiation. In step b) as well, radical formation and thus polymerisation is preferably initiated by radiation, particularly preferably by UV radiation.

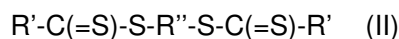
A preferred subject of the invention is therefore a method for producing a polymer system available in at least two phases, comprising the steps:

- a) UV-initiated RAFT polymerisation of a monomer composition I, comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, in order to form a polymerisate A; and
- b) UV-initiated RAFT polymerisation of a monomer composition II, comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, wherein at least 50 wt.% of the monomers in monomer composition II differ from those in monomer composition I, in the presence of polymerisate A in order to form polymerisate B, thereby obtaining a polymer system, available in at least two phases, comprising the polymerisates A and B;

characterised in that the RAFT polymerisations of steps a) and b) are carried out independently of one another in the presence of a RAFT controller substance which, in its original state, corresponds to the general structure (I)



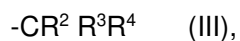
the general structure (II)



wherein

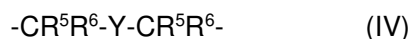
the substituents  $R'$  independently of one another represent an aryl, aralkyl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio, alkoxy, alkaryloxy or alkenoxy group or a group  $(NR^1)_2$ , wherein the substituents  $R^1$  independently of one another represent an alkyl or aryl group or, together with the N atom, form a heterocyclic ring containing 1 to 3 heteroatoms, independently selected from the group consisting of N, O and S;

R represents a sec- or tert-alkyl group, a cyano-sec-alkyl group, a cyano-tert-alkyl group, a carboxy-tert-alkyl group, a carboxy-sec-alkyl group, an aralkyl group or a group of the general structure (III)



wherein  $R^2$  represents an alkyl group or H,  $R^3$  represents a cyano, carboxy or carboxylic acid ester group, and  $R^4$  represents an aryl group; and

$R''$  represents a group of the general structure (IV)



wherein  $R^5$  and  $R^6$  independently represent a hydrogen atom, an n-alkyl group, a cyano group, a carboxy group or a carboxylic acid ester group, and

Y represents an alkylene or arylene group, or a group having a structure selected from  $-(CH_2)_m-CO-O-(CH_2)_n-O-CO-(CH_2)_m-$  and  $-(CH_2)_m-CO-NR^7-(CH_2)_n-NR^7-CO-(CH_2)_m-$ , wherein n represents an integer from 1 to 12; m represents 0 to 4; and  $R^7$  represents an organyl group.

The method according to the invention is intended to result in a polymer system available in at least two phases. Furthermore, it was an objective of the invention to provide the two- or multi-phase polymer system with the highest possible cohesion. It therefore appeared important, when selecting the monomers used in the two polymerisation steps, to take these and, where applicable, further properties of the final polymer system into account.

Against this background, in one embodiment of the invention, one of the monomer compositions I and II comprises in total at least 50 wt.%, more preferably in total at least 60 wt.%, in particular in total at least 75 wt.%, of one or more monomers having a glass transition temperature of the respective homopolymer of  $\leq 0^\circ\text{C}$ , more preferably of  $\leq -10^\circ\text{C}$ , in particular of  $\leq -20^\circ\text{C}$ ; and the other of the monomer compositions I and II comprises in total at least 60 wt.%, more preferably in total at least 70 wt.%, in particular in total at least 80 wt.%, of one or more monomers having a glass transition temperature of the respective homopolymer of  $\geq 50^\circ\text{C}$ , more preferably of  $\geq 75^\circ\text{C}$ , in particular of  $\geq 100^\circ\text{C}$ .

In a development of this embodiment, one of the monomer compositions I and II preferably comprises, in total, at least 50 wt.%, more preferably at least 60 wt.%, and in particular at least 75 wt.%, of one or more monomers selected from the group consisting of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, iso-amyl acrylate, n-hexyl acrylate, 2-heptyl acrylate, n-heptyl acrylate, 2-ethylhexyl acrylate, 2-octyl acrylate, n-octyl acrylate, iso-octyl acrylate, n-nonyl acrylate, iso-nonyl acrylate, n-decyl acrylate, iso-decyl acrylate, 2-[[[(butylamino)carbonyl]oxy]ethyl acrylate, 2-cyanoethyl acrylate, 2-(2-ethoxyethoxy)ethyl

acrylate, phenoxyethyl acrylate, iso-stearyl acrylate, docosyl acrylate, and 2-[2-(2-methoxyethoxy)ethoxy]ethyl acrylate; and

the other of the monomer compositions I and II comprises, in total, at least 60 wt.%, more preferably at least 70 wt.%, and in particular at least 80 wt.%, of one or more monomers selected from the group consisting of isobornyl acrylate, norbornyl acrylate, benzyl acrylate, 3,3,5-trimethylcyclohexyl acrylate, cyclohexyl acrylate, 4-[(6-acryloyloxy)hexyloxy]4'-cyanobiphenyl, N-succinimidyl acrylate, 1-ethylcyclopentyl acrylate, N-tert-octyl acrylamide, N-tert-butyl acrylamide, dimethyl acrylamide, diethylacrylamide, N-isopropylacrylamide, acrylamide, N-[3-(dimethylamino)propyl]acrylamide, diacetoneacrylamide, N-(butoxymethyl)acrylamide, N-phenylacrylamide, N-[2-(dimethylamino)ethyl]acrylamide, N-[2-(diethylamino)ethyl]acrylamide, methyl methacrylate, ethyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, isobornyl methacrylate, glycerol formal methacrylate, 2-dimethylaminoethyl methacrylate, phenoxyethyl methacrylate, 9-anthrylmethyl methacrylate, 2-ethyl-2-adamantyl methacrylate, 2-(acetoacetyloxy)ethyl methacrylate, 2-isopropyl-2-methacryloyloxyadamantane, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, furfuryl methacrylate, 2-methacryloyloxy-2-methyladamantane, 2-morpholinoethyl methacrylate, phenyl methacrylate, N-succinimidyl methacrylate, 2-(tert-butylamino)ethyl methacrylate, 2-cyclohexylpropan-2-yl methacrylate, 1-adamantyl methacrylate, 1-methylcyclopentyl methacrylate, 3-dimethylaminopropyl methacrylamide, N-tert-butyl methacrylamide, N-(methoxymethyl)methacrylamide, N,N-dimethylmethacrylamide, methacrylamide, N-phenylmethacrylamide, N,N-dimethylmethacrylamide, N-isopropylmethacrylamide, N-vinylformamide, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylcarbazole, N-vinylimidazole, vinylmethyloxazolidinone and N-vinyl-N-methylacetamide.

More preferably, one of the monomer compositions I and II comprises in total at least 50 wt.%, more preferably at least 60 wt.%, and in particular at least 75 wt.%, of one or more monomers selected from the group consisting of n-butyl acrylate, isoamyl acrylate, n-heptyl acrylate, 2-ethylhexyl acrylate, 2-octyl acrylate, iso-octyl acrylate, n-octyl acrylate, n-decyl acrylate and iso-decyl acrylate; and

the other of the monomer compositions I and II comprises in total at least 60 wt.%, more preferably at least 70 wt.%, and in particular at least 80 wt.%, one or more monomers selected from the group consisting of isobornyl acrylate, norbornyl acrylate, tert-butyl methacrylate, benzyl acrylate, N-isopropyl acrylamide, N-tert-octyl acrylamide, N-tert-butyl acrylamide and dimethyl acrylamide.

In a further development of this embodiment, one of the monomer compositions I and II preferably comprises in total at least 50 wt.%, more preferably in total at least 60 wt.%, and in particular in total at least 75 wt.%, of one or more monomers selected from the group consisting of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, iso-amyl acrylate, n-hexyl acrylate, n-heptyl acrylate, 2-heptyl acrylate, 2-ethylhexyl acrylate, 2-octyl acrylate, n-octyl acrylate, iso-octyl acrylate, n-nonyl acrylate, iso-nonyl acrylate, n-decyl acrylate, iso-decyl acrylate, 2-[[[(butylamino)carbonyl]oxy]ethyl acrylate, 2-cyanoethyl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, phenoxyethyl acrylate, iso-stearyl acrylate, docosyl acrylate, and 2-[2-(2-methoxyethoxy)ethoxy]ethyl acrylate;

up to a total of at most 35 wt.%, more preferably up to a total of at most 25 wt.%, and in particular up to a total of at most 20 wt.%, of one or more monomers selected from the group consisting of isobornyl acrylate, norbornyl acrylate, methyl methacrylate, dimethylacrylamide, diethylacrylamide, 4-tert-butylcyclohexyl acrylate, tert-butyl acrylate, tert-butyl methacrylate, cyclohexyl methacrylate and cyclohexyl acrylate; as well as

up to a total of at most 10 wt.% of one or more functionalised monomers; and

the other of the monomer compositions I and II comprises in total at least 60 wt.%, more preferably in total at least 70 wt.%, and in particular in total at least 80 wt.%, of one or more monomers selected from the group consisting of isobornyl acrylate, norbornyl acrylate, benzyl acrylate, 3,3,5-trimethylcyclohexyl acrylate, cyclohexyl acrylate, 4-[(6-acryloyloxy)hexyloxy]4'-cyanobiphenyl, N-succinimidyl acrylate, 1-ethylcyclopentyl acrylate, N-tert-octyl acrylamide, N-tert-butyl acrylamide, dimethyl acrylamide, diethyl acrylamide, N-isopropyl acrylamide, N-hydroxyethylacrylamide, acrylamide, N-[3-(dimethylamino)propyl]acrylamide, diacetoneacrylamide, N-(butoxymethyl)acrylamide, N-phenylacrylamide, N-[2-(dimethylamino)ethyl]acrylamide, N-[2-(diethylamino)ethyl]acrylamide, methyl methacrylate, ethyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, isobornyl methacrylate, glycerol formal methacrylate, 2-dimethylaminoethyl methacrylate, phenoxyethyl methacrylate, 9-anthrylmethyl methacrylate, 2-ethyl-2-adamantyl methacrylate, 2-(acetoacetyloxy)ethyl methacrylate, 2-isopropyl-2-methacryloyloxyadamantane, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, furfuryl methacrylate, 2-methacryloyloxy-2-methyladamantane, 2-morpholinoethyl methacrylate, phenyl methacrylate, N-succinimidyl methacrylate, 2-(tert-butylamino)ethyl methacrylate, 2-cyclohexylpropan-2-yl methacrylate, 1-adamantyl methacrylate, 1-methylcyclopentyl methacrylate, 3-dimethylaminopropyl methacrylamide, N-tert-butyl methacrylamide, N-(methoxymethyl)methacrylamide, N,N-

dimethylmethacrylamide, N-phenylmethacrylamide, N,N-dimethylmethacrylamide, N-isopropylmethacrylamide, N-vinylformamide, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylcarbazole, N-vinylimidazole, vinylmethyloxazolidinone and N-vinyl-N-methylacetamide; as well as

up to a total of at most 10 wt.% of one or more functionalised monomers,

wherein the functionalised monomers are selected from the group consisting of hydroxyethyl acrylate, hydroxypropyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, 4-hydroxyethylacrylamide, acrylic acid, methacrylic acid, 2-acryloyloxyethylsuccinate, methacryloyloxyethylsuccinate, sulfoethyl methacrylate, acrylamide, methacrylamide, glycidyl acrylate, glycidyl methacrylate, 3,4-epoxycyclohexyl methyl acrylate, 3,4-epoxycyclohexyl methyl methacrylate, 4-hydroxybutyl acrylate glycidyl ether, 4-hydroxybutyl methacrylate glycidyl ether, isocyanatoethyl acrylate, isocyanatoethyl methacrylate, 2-[2-(methacryloyloxy)ethyloxy]ethyl isocyanate, 2-[2-(acryloyloxy)ethyloxy]ethyl isocyanate and  $\alpha,\alpha$ -dimethyl-m-isopropenylbenzyl isocyanate.

In particular, one of the monomer compositions I and II comprises in total at least 50 wt.%, more preferably in total at least 60 wt.%, and in particular in total at least 75 wt.%, of one or more monomers selected from the group consisting of n-butyl acrylate, isoamyl acrylate, n-heptyl acrylate, 2-ethylhexyl acrylate, 2-octyl acrylate, iso-octyl acrylate, n-octyl acrylate, n-decyl acrylate and iso-decyl acrylate;

up to a total of at most 35 wt.%, more preferably up to a total of at most 25 wt.%, and in particular up to a total of at most 20 wt.%, of one or more monomers selected from the group consisting of isobornyl acrylate, norbornyl acrylate, methyl methacrylate, dimethylacrylamide, and

up to a total of at most 10 wt.% of one or more monomers selected from the group consisting of acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, 3,4-epoxycyclohexyl methyl acrylate, 3,4-epoxycyclohexyl methyl methacrylate, glycidyl acrylate and glycidyl methacrylate; and

the other of the monomer compositions I and II comprises in total at least 60 wt.%, more preferably in total at least 70 wt.%, and in particular in total at least 80 wt.%, of one or more monomers selected from the group consisting of isobornyl acrylate, norbornyl acrylate, tert-

butyl methacrylate, benzyl acrylate, N-isopropylacrylamide, N-tert-octylacrylamide, N-tert-butylacrylamide and dimethylacrylamide; as well as

up to a total of at most 10 wt.% of one or more monomers selected from the group consisting of acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, 3,4-epoxycyclohexyl methyl acrylate, 3,4-epoxycyclohexyl methyl methacrylate, glycidyl acrylate and glycidyl methacrylate.

In a specific embodiment of the method according to the invention, at least the monomer composition II is free from methyl methacrylate; more preferably, it is free from methacrylic acid esters and methacrylamides; in particular, it is free from any methacrylic compounds.

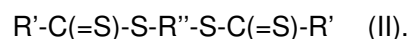
It is also preferred that monomer composition I is free of methyl methacrylate; more preferably, it is free of methacrylic acid esters and methacrylamides; in particular, it is free of any methacrylic compounds.

It has been shown that the exclusion of the aforementioned compounds has a beneficial effect on the polymerisation rate.

According to the invention, the polymerisations of steps a) and b) take place independently of one another in the presence of a specific RAFT controller substance which, in its original state, corresponds to the general structure (I)



the general structure (II)



'In its original state' here means that the controller substance in question is considered without any component of the polymer chain associated with it from the start of polymerisation resulting from the monomers used.

In the general structures (I) and (II), the substituents R' represent, independently of one another, preferably an aryl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio or alkoxy group, or a group (NR<sup>1</sup>)<sub>2</sub>, wherein the substituents R<sup>1</sup>

independently represent an aryl group. More preferably, the n-alkyl groups contained in the aforementioned substituents are C<sub>3</sub>-C<sub>20</sub>-n-alkyl groups, in particular C<sub>10</sub>-C<sub>15</sub>-n-alkyl groups; and the aryl groups are phenyl groups.

In the general structure (IV), Y is preferably an alkylene or arylene group, more preferably an arylene group and particularly preferably a phenylene group.

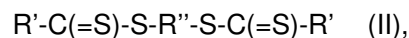
A further preferred subject of the invention is, in this respect, a method for producing a polymer system comprising at least two phases, comprising the steps:

- a) UV-initiated RAFT polymerisation of a monomer composition I, comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, in order to form a polymerisate A; and
- b) UV-initiated RAFT polymerisation of a monomer composition II, comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, wherein at least 50 wt.% of the monomers in monomer composition II differ from those in monomer composition I, in the presence of polymerisate A, in order to form polymerisate B, thereby obtaining a polymer system, available in at least two phases, comprising the polymerisates A and B;

characterised in that the RAFT polymerisations of steps a) and b) are carried out independently of one another in the presence of a RAFT controller substance which, in its original state, corresponds to the general structure (I)



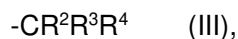
the general structure (II)



wherein

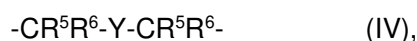
the substituents R' independently of one another represent an aryl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio or alkoxy group or a group (NR<sup>1</sup>)<sub>2</sub> in which the substituents R<sup>1</sup> independently of one another represent an aryl group;

R represents a sec- or tert-alkyl group, a cyano-sec-alkyl group, a cyano-tert-alkyl group, a carboxy-tert-alkyl group, a carboxy-sec-alkyl group, an aralkyl group or a group of the general structure (III)



wherein  $\text{R}^2$  represents an alkyl group or H,  $\text{R}^3$  represents a cyano, carboxy or carboxylic acid ester group, and  $\text{R}^4$  represents an aryl group; and

$\text{R}''$  represents a group of the general structure (IV)

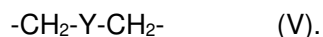


wherein  $\text{R}^5$  and  $\text{R}^6$  independently represent a hydrogen atom, an n-alkyl group, a cyano group, a carboxy group or a carboxylic acid ester group, and

Y represents an arylene group.

In one embodiment of the invention, the RAFT controller substance in its original state corresponds to the general structure (I),  $\text{R}'$  represents an aryl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio or alkoxy group or a group  $(\text{NR}^1)_2$ , wherein the substituents  $\text{R}^1$  independently represent an aryl group; the n-alkyl groups are preferably  $\text{C}_3\text{-C}_{20}$  -n-alkyl groups, in particular  $\text{C}_{10}\text{-C}_{15}$ -n-alkyl groups, the aryl groups are preferably phenyl groups; and R represents a cyano-tert-alkyl group, a carboxy-tert-alkyl group or a benzylthio group.

In a further embodiment, the RAFT controller substance in its original state corresponds to the general structure (II), in which the substituents  $\text{R}'$  are identical. Preferably, the substituents  $\text{R}'$  each represent an aryl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio or alkoxy group, or a group  $(\text{NR}^1)_2$ , wherein the substituents  $\text{R}^1$  independently of one another represent an aryl group. More preferably, the n-alkyl groups contained in the aforementioned substituents are  $\text{C}_3\text{-C}_{20}$ -n-alkyl groups, in particular  $\text{C}_{10}\text{-C}_{15}$ -n-alkyl groups; and the aryl groups are phenyl groups. Independently of or in combination with the preferred substituents described herein,  $\text{R}''$  in this embodiment represents a group of the general structure (V)



Y therein preferably represents an arylene group and, more preferably, a phenylene group.

In one embodiment of the method according to the invention, at least the RAFT polymerisation of step b) is carried out in a solvent, and the method comprises

- c) the removal of the solvent under the influence of temperature.

A significant advantage of the method according to the invention is that the polymers produced in steps a) and b) can undergo this step without significant loss of cohesion, regardless of the apparatus used for removing the solvent. Preferably, the removal of the solvent takes place in an extruder.

A further object of the invention is a polymer system available in at least two phases, which can be produced by a method according to the invention. Preferably, the polymer system producible by a method according to the invention is a block copolymer. The polymer blocks of this block copolymer are preferably formed by the polymerisates A and B. It is more preferable that the polymer system obtainable by a method according to the invention is a triblock copolymer, in particular a triblock copolymer of the form ABA or BAB, wherein A and B denote the polymerisates A and B.

Polymer systems according to the invention are characterised, inter alia, by the fact that they withstand exposure to high temperatures, such as those used in particular for the removal of solvents in concentration extruders and similar apparatus, but also during further processing, for example by means of extrusion, without significant loss of cohesion. Without wishing to be bound by this theory, the inventors assume that the selection of the RAFT controller substances used in the method of the invention ensures that, at the end of polymerisation, the RAFT controller substances are not located within the polymer chains but are terminal. Since the RAFT controller substances are the most thermally unstable structures within the polymer systems, their decomposition under thermal stress does not, for this reason, lead to polymer degradation and the associated loss of cohesion, as would be expected if the RAFT controller substance structures were located within the polymer chains.

Due to their cohesive stability, polymer systems according to the invention are preferably used as a component of a pressure-sensitive adhesive compound, which is produced by thermomechanical mixing of its underlying components, as occurs, for example, in an extruder. A further object of the invention is therefore the use of a polymer system according to the invention as a component for the production of a pressure-sensitive adhesive by means of a process comprising thermomechanical mixing of the components to produce the pressure-sensitive adhesive.

According to technical understanding, a pressure-sensitive adhesive is an adhesive that possesses pressure-sensitive properties, i.e. the ability to form a permanent bond with a substrate even under relatively light pressure. Such adhesives or pressure-sensitive adhesive tapes are generally permanently self-adhesive even at room temperature, which means that they exhibit a certain viscosity and tackiness, enabling them to wet the surface of a substrate even under light pressure. Without wishing to be bound by this theory, it is often assumed that a pressure-sensitive adhesive can be regarded as an extremely high-viscosity liquid with an elastic component, which consequently exhibits characteristic viscoelastic properties leading to the permanent self-adhesiveness and pressure-sensitive adhesive properties described above. It is assumed that, in pressure-sensitive adhesives, mechanical deformation gives rise to both viscous flow processes and the build-up of elastic restoring forces. The viscous flow component serves to achieve adhesion, whilst the elastic restoring forces are necessary, in particular, to achieve cohesion. The relationships between rheology and pressure-sensitive adhesion are known in the prior art and are described, for example, in 'Satas, Handbook of Pressure Sensitive Adhesives Technology', Third Edition, (1999), pages 153 to 203. To characterise the extent of the elastic and viscous components, the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) are usually employed; these can be determined by means of dynamic mechanical analysis (DMA), for example using a rheometer. In the context of the present invention, an adhesive composition is preferably understood to be pressure-sensitive and thus a pressure-sensitive adhesive if, at a temperature of 23°C in the deformation frequency range from  $10^0$  to  $10^1$  rad/sec,  $G'$  and  $G''$  each lie at least partly in the range from  $10^3$  to  $10^7$  Pa.

In the apparatus used to produce the pressure-sensitive adhesive, which may, for example, be an extruder, further process steps such as mixing with additives, filtration or degassing may also take place. The pressure-sensitive adhesive obtained in this way can be formed into a desired layer shape, for example by means of a calender, onto a substrate or a release liner.

During the processing of a polymer system according to the invention into a pressure-sensitive adhesive, the polymer system may be mixed with further components. These further components may be selected from the group consisting of further polymers; tack-enhancing resins; fillers, for example electrically conductive fillers, thermally conductive fillers and the like; flame retardants, for example ammonium polyphosphate and its derivatives; foaming agents; anti-ageing agents; light stabilisers; plasticisers and compounding particles.

### Examples

#### Measurement and test methods:

##### Method 1 – Determination of the glass transition temperature of polymers

The static glass transition temperature of the polymers was determined using dynamic scanning calorimetry (DSC). To do this, 5 mg of an untreated sample of the polymer in question was weighed into an aluminium crucible (volume 25  $\mu$ l) and sealed with a perforated lid. A DSC 204 F1 from Netzsch was used for the measurement. The experiment was carried out under nitrogen for inerting. The sample was first cooled to  $-150^{\circ}\text{C}$ , then heated at a rate of 10 K/min to  $+150^{\circ}\text{C}$  and cooled again to  $-150^{\circ}\text{C}$ . The subsequent second heating curve was again run at 10 K/min and the change in heat capacity recorded. Glass transitions are identified as steps in the thermogram (heat flow-temperature diagram, see Figure 1).

The glass transition temperature  $T_g$  was obtained as follows (see Figure 1):

The respective linear sections of the measurement curve before and after the step are extended in the direction of rising (section before the step) or falling (section after the step) temperatures (extended lines ① and ②). In the region of the step, a fitting line ⑤ is drawn parallel to the y-axis so that it intersects the two extended lines, in such a way that two areas ③ and ④ (between the respective extended line, the fitting line and the measurement curve) of equal area are formed. The point of intersection of the fitting line positioned in this way with the measurement curve gives the glass transition temperature.

##### Method 2 – Determination of molar masses

The values for the weight-average molar mass  $M_w$  given in this paper refer to the well-established determination by gel permeation chromatography (GPC). The determination is carried out on 100  $\mu$ l of a clear-filtered sample (sample concentration 3 g/l). Tetrahydrofuran is used as the eluent. The measurement is carried out at 25°C.

A PSS-SDV column, 5  $\mu$ m,  $10^3$  Å, 8.0 mm  $\times$  50 mm (specifications here and below in the order: type, particle size, internal diameter  $\times$  length; 1 Å =  $10^{-10}$  m) is used as a precolumn. For separation, a combination of PSS SDV columns, 5  $\mu$ m,  $10^3$  Å,  $10^5$  Å and  $10^6$  Å, each 8.0 mm  $\times$  300 mm, is used (columns from Agilent; detection via PSS SECcurity<sup>2</sup> differential refractometer). The flow rate is 1.0 ml per minute. Calibration is carried out using the commercially available ReadyCal-Kit Poly(styrene) high from Agilent. This is universally converted to polymethyl methacrylate (PMMA) using the Mark-Houwink parameters K and alpha, so that the data is reported in PMMA mass equivalents.

The polydispersity index (PDI) is determined, as is known to those skilled in the art, as the ratio of the weight-average to the number-average molecular weight.

### Method 3 – Dynamic Mechanical Analysis (DMA)

$G'$  and  $G''$  are determined using a rheometer. The material under investigation is subjected to a sinusoidally oscillating shear stress in a plate-plate configuration. In shear stress-controlled instruments, the deformation is measured as a function of time, along with the time lag of this deformation relative to the application of the shear stress. This time lag is referred to as the phase angle  $\delta$ .

The storage modulus  $G'$  is defined as follows:  $G' = (\tau/\gamma) \cdot \cos(\delta)$  ( $\tau$  = shear stress,  $\gamma$  = strain,  $\delta$  = phase angle = phase shift between the shear stress vector and the strain vector). The definition of the loss modulus  $G''$  is:  $G'' = (\tau/\gamma) \cdot \sin(\delta)$  ( $\tau$  = shear stress,  $\gamma$  = strain,  $\delta$  = phase angle = phase shift between the shear stress and strain vectors).

$$\tan \delta = G''/G'.$$

Instrument: strain-controlled rheometer (ARES), plate-plate,  $\varnothing$  25 mm

Deformation: 1 %

Frequency: 10 rad/s.

#### Method 4 – Determination of static shear strength (shear life)

Shear strength is a measure of the internal strength of the adhesive and was tested in the so-called static shear test as follows, with the influence of a preceding thermal load also being investigated:

The test was carried out under standard conditions (23°C, 50 % relative humidity) using a weight of 1 kg.

A 1.3 cm wide strip of the sample (50 µm polymer layer on 36 µm etched PET film) was bonded to a polished steel plate over a length of 2 cm by rolling over it with a 2 kg roller (twice back and forth). The samples produced in this way were stored for 6 hours in an oven at 200°C and then equilibrated for 30 minutes under test conditions but without a load. The test weight (1 kg) was then attached so that a shear stress parallel to the bonded surface was created, and the time until the bond failed was measured. The measurement result is given in minutes. The median of three individual measurements is reported.

#### Production of polymerisate A

A 3-litre vessel, of the type conventionally used for radical polymerisations, was filled with 900 g of isobornyl acrylate (IBOA), 10.395 g of dibenzyl trithiocarbonate (DBTTC) and 900 g of ethyl acetate (EtAc). After passing nitrogen gas through the mixture for 45 minutes whilst stirring, the reactor contents were heated to 58°C and 1.376 g of Vazo® 67 was added. The reactor contents were then heated further to 65°C. After a reaction time of 24 hours, the reactor contents were cooled to 35°C. The conversion was > 95% and the weight fraction of polymerisate A in the polymer solution was 50%.

#### Production of polymerisate B

A 3-litre vessel, conventional for radical polymerisations, was filled with 447.6 g of the polymerisate A solution, 676.2 g of n-butyl acrylate (nBA) and 676.2 g of ethyl acetate (EtAc). After passing nitrogen gas through the mixture for 45 minutes whilst stirring, the reactor contents were heated to 58°C and 0.258 g of Vazo® 67 was added. The reactor contents were then further heated to 65°C under a flow of nitrogen gas (). After 5 hours, the mixture was

diluted with 300 g of ethyl acetate. After a reaction time of 24 h, the reactor contents were cooled to 35°C. The conversion was > 98 %.

#### Production of polymerisate C

A 3-litre vessel, conventional for radical polymerisations, was filled with 900 g of n-butyl acrylate (nBA) and 3.933 g of 1,4-phenylene bis(methylene) didodecyl dicarbonotrithioate (BM1812®), as well as 900 g of ethyl acetate (EtAc). After passing nitrogen gas through the mixture for 45 minutes whilst stirring, the reactor contents were heated to 58°C and 0.229 g of Vazo® 67 was added. The reactor contents were then heated further to 65°C. After a reaction time of 24 hours, the reactor contents were cooled to 35°C. The conversion was > 95% and the weight fraction of polymerisate A in the polymer solution was 50%.

#### Production of polymerisate D

A 3-litre vessel, conventional for radical polymerisations, was filled with 1350 g of the polymer solution of polymer C, 225 g of iso-bornyl acrylate (IBOA) and 225 g of ethyl acetate (EtAc). After passing nitrogen gas through the mixture for 45 minutes whilst stirring, the reactor contents were heated to 58°C and 0.172 g of Vazo® 67 was added. The reactor contents were then heated further to 65°C. After 5 hours, the mixture was diluted with 300 g of ethyl acetate. After a reaction time of 24 hours, the contents of the reactor were cooled to 35°C. The conversion was > 98 %.

$M_w$  = 706,000 g/mol; PDI = 10.22

Table 1: Weight-average molecular weight, polydispersity and shear life of the polymerisates

| Polymerisate | $M_w$ [g/mol] | PDI   | Shear life [min] |
|--------------|---------------|-------|------------------|
| A            | 44,000        | 1.70  |                  |
| B            | 176,000       | 1.83  | < 1              |
| C            | 238,000       | 1.46  |                  |
| D            | 706,000       | 10.22 | > 10,000         |

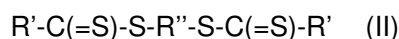
## Claims

1. A method for producing a polymer system available in at least two phases, comprising the following steps:
  - a) RAFT polymerisation of a monomer composition I comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group to form a polymerisate A; and
  - b) RAFT polymerisation of a monomer composition II comprising in total at least 80 wt.% of one or more monomers selected from the group consisting of methacrylic acid esters, methacrylamides and monomers with at least one polymerisable vinyl group, wherein the monomer composition II differs in at least 50 wt.% of its monomers from the monomer composition I, in the presence of polymerisate A to form polymerisate B, thereby obtaining a polymer system, available in at least two phases, comprising polymerisate A and B;

characterised in that the RAFT polymerisations of steps a) and b) are carried out independently of one another in the presence of a RAFT controller substance which, in its original state, has the general structure (I)



the general structure (II)



wherein

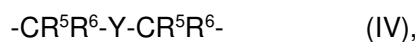
the substituents  $R'$  independently of one another represent an aryl, aralkyl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio, alkoxy, alkaryloxy or alkenoxy group or a group  $(NR^1)_2$ , wherein the substituents  $R^1$  independently of one another represent an alkyl or aryl group or, together with the N atom, form a heterocyclic ring containing 1 to 3 heteroatoms, independently selected from the group consisting of N, O and S;

R represents a sec- or tert-alkyl group, a cyano-sec-alkyl group, a cyano-tert-alkyl group, a carboxy-tert-alkyl group, a carboxy-sec-alkyl group, an aralkyl group or a group of the general structure (III)



wherein  $\text{R}^2$  represents an alkyl group or H,  $\text{R}^3$  represents a cyano, carboxy or carboxylic acid ester group, and  $\text{R}^4$  represents an aryl group; and

$\text{R}''$  represents a group of the general structure (IV)

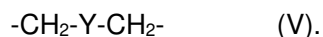


wherein  $\text{R}^5$  and  $\text{R}^6$  independently represent a hydrogen atom, an n-alkyl group, a cyano group, a carboxy group or a carboxylic acid ester group; and

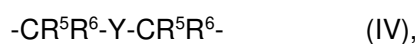
Y represents an alkylene or arylene group, or a group having a structure selected from  $-(\text{CH}_2)_m-\text{CO}-\text{O}-(\text{CH}_2)_n-\text{O}-\text{CO}-(\text{CH}_2)_m-$  and  $-(\text{CH}_2)_m-\text{CO}-\text{NR}^7-(\text{CH}_2)_n-\text{NR}^7-\text{CO}-(\text{CH}_2)_m-$ , wherein n represents an integer from 1 to 12; m represents 0 to 4; and  $\text{R}^7$  represents an organyl group.

2. The method according to claim 1, characterised in that the substituents  $\text{R}'$  independently of one another represent an aryl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio or alkoxy group or a group  $(\text{NR}^1)_2$ , wherein the substituents  $\text{R}^1$  independently of one another represent an aryl group.
3. The method according to claim 2, characterised in that the RAFT controller substance, in its original state, corresponds to the general structure (I), wherein R represents a cyano-tert-alkyl group, a carboxy-tert-alkyl group or a benzylthio group.
4. The method according to claim 1, characterised in that the RAFT controller substance, in its original state, corresponds to the general structure (II), wherein the substituents  $\text{R}'$  are identical.
5. The method according to claim 4, characterised in that the substituents  $\text{R}'$  each represent an aryl, n-alkylthio, carboxy-n-alkylthio, carboxylic acid ester-n-alkylthio, hydroxy-n-alkylthio, arylthio or alkoxy group, or a group  $(\text{NR}^1)_2$ , wherein the substituents  $\text{R}^1$  independently of one another represent an aryl group.

6. The method according to any one of claims 4 and 5, characterised in that R" represents a group of the general structure (V)



7. The method according to any one of claims 4 to 6, characterised in that R" represents a group of the general structure (IV)



wherein Y represents an arylene group.

8. The method according to any one of the preceding claims, characterised in that at least the RAFT polymerisation of step b) is carried out in a solvent and the method comprises
- c) the removal of the solvent under the influence of temperature.
9. A polymer system available in at least two phases, producible by a method according to any one of claims 1 to 8.
10. Use of a polymer system according to claim 9 as a component for producing a pressure-sensitive adhesive by means of a method comprising thermomechanical mixing of the components to produce the pressure-sensitive adhesive .