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Amphiphilic segmented polymer networks based on poly(2-alkyl-2-oxazoline) and poly(methyl methacrylate)

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Abstract

Amphiphilic segmented polymer networks (SPNs) have been prepared by free radical copolymerization of methyl methacrylate with α,ω-bisacrylate terminated poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline). DSC and DMTA analysis demonstrated the influence of the copolymer composition, the molecular weight and nature of the poly(2-alkyl-2-oxazoline)s and the polymerization conditions on the final phase morphology of the networks. A comparative phase morphology study of the polymer blends and SPNs revealed the more compatible phase morphology of the networks. The compatibility could be further increased by UV-induced network formation. The investigation of the solvent uptake in different solvents clearly demonstrated the amphiphilic nature of the SPNs. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Segmented polymer network; Poly(alkyloxazoline); Amphiphilic

1. Introduction

Multicomponent and multiphase polymer systems are of considerable interest for specific applications as high performance materials. A variety of structures have been developed to achieve multicomponent chain topologies such as block copolymers, graft copolymers, interpenetrating and semi-interpenetrating polymer networks [1–3]. A relatively new way to combine two polymers in one material is the synthesis of segmented polymer networks (SPNs). These network structures, in which polymer A acts as a macromolecular cross-linker for polymer B, demonstrate an interesting multicomponent topology that can be considered as an intermediate between graft copolymers and interpenetrating networks [4–6]. For the synthesis of these materials, copolymerization of bifunctional macromonomers is mostly applied. Recently, some papers have been published on the synthesis and properties of amphiphilic copolymer networks obtained by combining either a hydrophobic bifunctional macromonomer with a hydrophilic comonomer [7–9] or vice versa [10–12]. By proper combinations of the bis-macromonomer and the comonomer, it is possible to obtain networks with well-defined segmented structure, a wide range of mechanical properties and adjustable hydrophilic-hydrophobic balance.

In a previous paper [13], the synthesis of poly(2-alkyl-2-oxazoline) bis-macromonomers (alkyl = methyl, ethyl) and the corresponding homopolymer networks have been reported. In the present work, we have extended our approach to segmented copolymer networks by copolymerizing polyoxazoline α,ω-diacrylates with methyl methacrylate (MMA). Series of networks with different compositions and molecular weights of the polyoxazolines have been prepared and the phase morphology of the products has been studied by DSC and DMTA. In order to evaluate the amphiphilic character of these new materials, their swelling behaviour has been investigated in solvents with different polarities.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Aldrich) was purified by distillation in the presence of a radical inhibitor, phenothiazine (Aldrich). The initiators 1,1′-azobisisobutyronitrile (AIBN, Aldrich) and 1-methylsulphonic ester of methylolbenzoine (MSMB, Akzo) were used as received.

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Other reagents and solvents were purified by the usual procedures.

Poly(2-alkyl-2-oxazoline) bis-macromonomers were synthesized as described in Ref. [13]. Briefly, 2-methyl-2-oxazoline (MeOx) and 2-ethyl-2-oxazoline (EtOx) have been polymerized in acetonitrile at 70 °C using the bifunctional initiator 1,4-dibromo-2-butene. Acrylate groups were introduced by end capping the living oxazolinium species with acrylic acid in the presence of a proton scavenger. In this work, PMeOx α,ω-diacrylate of $M_n = 2800\ \mathrm{g\ mol^{-1}}$ and PEtOx α,ω-diacrylates of $M_n =$ 2500 and 4300 $\mathrm{g\ mol^{-1}}$ were used.

2.2. Synthesis of the copolymer networks

Chosen amounts of MMA and bis-macromonomer were mixed under nitrogen and methanol was added dropwise until a clear homogeneous solution was obtained. Then, 0.5 mol% of AIBN (with respect to MMA) was added, the reaction mixture was stirred for several minutes and transferred by means of a syringe in a mould composed of two glass plates separated by a silicon spacer (1 mm). Before use, the glass plates were treated consecutively with concentrated H_2SO_4 and 10% toluene solution of trimethylsilylchloride for hydrophobization. The mould was kept in an oven at 60 °C for 12 h. After removal of the glass plates, the film obtained was dried at 70 °C under vacuum for 24 h.

The same procedure was followed in the case of UV-polymerization, using 0.5 mol% of the initiator MSMB and irradiating the mould with UV light (360 nm; 10 mW $\mathrm{cm^{-2}}$) for 30 min.

2.3. Measurements

DSC analyses were carried out on a Perkin–Elmer 7 equipment provided with TAC 7/DX thermal controller at a scanning rate of 10 °C $\mathrm{min^{-1}}$. The measurements were taken over a temperature range of 0–150 °C. Each DSC testing cycle consisted of heating, cooling and repeating scans. The glass temperatures (T_g) were taken as the midpoints of the change in heat capacity. Values of E', E'' and tan δ were measured by a DMA 2980 instrument from TA-Instruments on rectangular films of 1 mm thickness at a heating rate of 2 °C $\mathrm{min^{-1}}$ and a frequency of 1 Hz.

Swelling studies for networks were done gravimetrically. In a typical case, a disc cut from the network film was weighed and transferred into the required medium. At regular intervals, the disc was taken out, the excess solvent was removed from the surface with tissue paper, the disc was weighed and then returned to the medium. The solvent uptake was continued until constant weight was attained. The equilibrium degree of solvent weight uptake, Q, was calculated from Eq. (1), where w_0 is the initial weight of the dry sample and w_e is the final weight of the swollen sample.

To determine the soluble fraction of a network, a sample was extracted with the corresponding solvent in a Soxhlet extraction apparatus for 8 h and then dried at 70 °C under vacuum until constant weight. The soluble fraction, S, was calculated from Eq. (2), where w_0 is the initial weight of the dry sample and w is the weight of the dry sample after the extraction

$$Q\,(\%) = 100\frac{w_e - w_0}{w_0} \tag{1}$$

$$S\,(\%) = 100\frac{w_0 - w}{w_0} \tag{2}$$

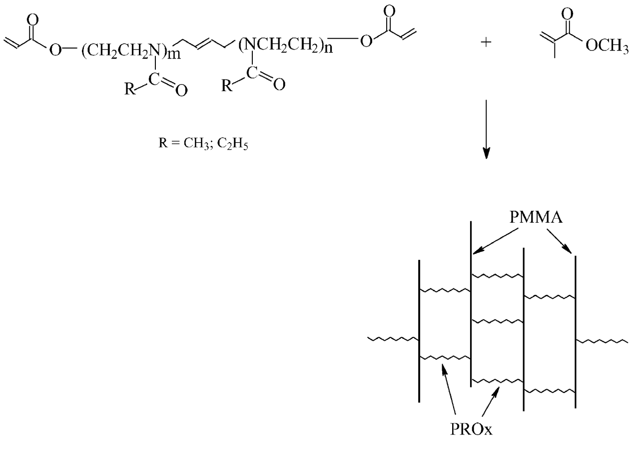
3. Results and discussion

3.1. Synthesis of poly(2-alkyl-2-oxazoline)–poly(methyl methacrylate) (PROx–PMMA) copolymer networks

The radical copolymerization of polyoxazoline bis-macromonomers with MMA to the corresponding segmented copolymer networks is represented in Scheme 1.

An important requirement for such kind of reaction is the homogeneity of the reaction mixture. Preliminary tests revealed that bis-macromonomers of both 2-methyl- and 2-ethyloxazoline of molecular weights up to 5000 do not dissolve in MMA. Therefore, small amounts of methanol were added to ensure homogeneous reaction mixtures. The copolymerizations were carried out under two different reaction conditions: (1) at 60 °C in the presence of AIBN as initiator and (2) UV-induced copolymerization at room temperature with MSMB as photo-initiator. Series of networks were prepared, in which the polyoxazoline content varied from 20 to 70 wt%. The final products were transparent hygroscopic films, which were brittle in the dry state.

Tables 1 and 2 give a survey of the soluble fractions in water (good solvent for polyoxazolines) and acetone (good solvent for PMMA) as a function of the composition of the initial reaction mixture. The soluble fraction generally increases for higher fractions of the bis-macromonomers. This is explained by taking into account the lower



Scheme 1. Reaction scheme for the synthesis of the segmented networks.

Table 1
Soluble fraction (S) and T_g of SPNs based on PMeOx2800 bis-macromonomers

Code[a]	S in water (wt%)	S in acetone (wt%)	T_g (DSC) (°C)
PMeOx$_{20}$−PMMA	5	2	43; 95
PMeOx$_{30}$−PMMA	10	0	42; 94
PMeOx$_{40}$−PMMA	13	4	38; 89
PMeOx$_{50}$−PMMA	17	3	48
PMeOx$_{70}$−PMMA	22	9	36; 83

[a] The index after the abbreviation PMeOx denotes the weight fraction of the bis-macromonomer in the initial reaction mixture.

concentration of the polymerizable end-groups of the macromonomer and the higher segment density around the propagating radicals [14]. The relatively high soluble fractions indicate that, although the reactive functions in the bis-macromonomer (acrylate end groups) and in the comonomer (MMA) have a similar chemical structure and the methanol, added as common solvent, solubilizes the reaction mixture, the repulsion between growing PMMA and macromonomer chains leads to incomplete consumption of the macromonomer. Indeed, ^{1}H NMR analyses proved the presence of unreacted macromonomer in the soluble fractions together with non-cross-linked PMMA and non-polymerized monomer MMA.

3.2. Bulk properties

Generally, polymers built of different segments exhibit a pronounced tendency for phase separation, which results in different morphologies depending on the copolymer composition and structure [15]. In the segmented copolymer networks, however, the chain mobility of the segments is strongly restricted due to the presence of chemical bonds introduced by cross-linking. Therefore, suppressed phase separation and improved compatibility could be expected for such networks.

Table 2
Soluble fraction (S) and T_g of SPNs based on PEtOx bis-macromonomers

Code[a]	S in water (wt%)	S in acetone (wt%)	T_g (DSC) (°C)
PEtOx2500$_{30}$−PMMA	5	4	78
PEtOx2500$_{40}$−PMMA	13	8	60
PEtOx2500$_{50}$−PMMA	18	17	52
PEtOx2500$_{70}$−PMMA	26	16	51
PEtOx4300$_{20}$−PMMA	4	15	102
PEtOx4300$_{30}$−PMMA	3	1	81
PEtOx4300$_{50}$−PMMA	17	4	55
PEtOx4300$_{70}$−PMMA	16	6	48
PEtOx2500$_{50}$−PMMA[b]	11	15	37
PEtOx4300$_{50}$−PMMA[b]	6	5	42

[a] The number after the abbreviation PEtOx denotes the M_n of the bis-macromonomer used, the index its wt% in the initial reaction mixture.

[b] UV-induced polymerization.

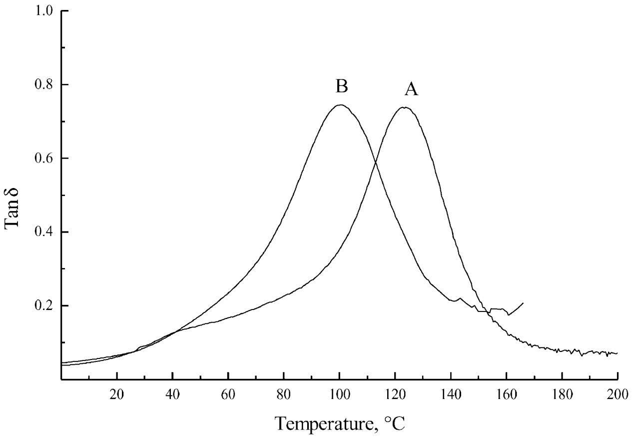


Fig. 1. tan δ versus temperature of SPNs (A) PMeOx2800$_{30}$−PMMA and (B) PMeOx2800$_{50}$−PMMA.

A number of papers deal with the miscibility of polyoxazolines with commodity polymers such as polypropylene, polystyrene, poly(vinyl chloride) [16–18] but, to the best of our knowledge, no data have been published on the miscibility of PMeOx or PEtOx with PMMA. Therefore, polyoxazoline–PMMA blends were prepared by polymerizing MMA in the presence of PMeOx and PEtOx (without polymerizable end groups) at the same reaction conditions as used for the network preparation. DSC measurements of the blend containing equal amounts of both polymers prove the occurrence of phase separation in PMeOx–PMMA and PEtOx–PMMA blends. The DSC spectra display two distinct glass transitions, i.e. one at lower temperature corresponding to the T_g of the polyoxazoline, and a second one at 105–115 °C corresponding to the T_g of PMMA. DSC measurements of the PMeOx–PMMA SPNs also display two glass transitions but they are shifted inwards compared to those of the corresponding polymer blends (Table 1). This observation is already a first indication of the more compatible phase morphology of the network structures. Moreover, in the networks with a PMeOx content of 50 wt%, only one single, broad glass transition could be observed in the DSC-spectrum.

The same materials were also analysed by means of DMTA (Fig. 1). The tan δ–T curve of the network with low PMeOx content (curve A) shows a main transition at 120 °C, corresponding to the T_g of PMMA, and a shoulder at about 45 °C, which is close to the T_g of PMeOx. In contrast, the sample with 50 wt% PMeOx (curve B) exhibits a broad but essentially single T_g situated between the T_gs of the homopolymers, which confirms its higher degree of compatibility as observed by DSC measurements.

In contrast to the PMeOx-containing networks, all PEtOx–PMMA copolymer networks exhibit single transitions in the DSC curves at decreasing temperatures with increasing PEtOx-fraction (Table 2 and Fig. 2).

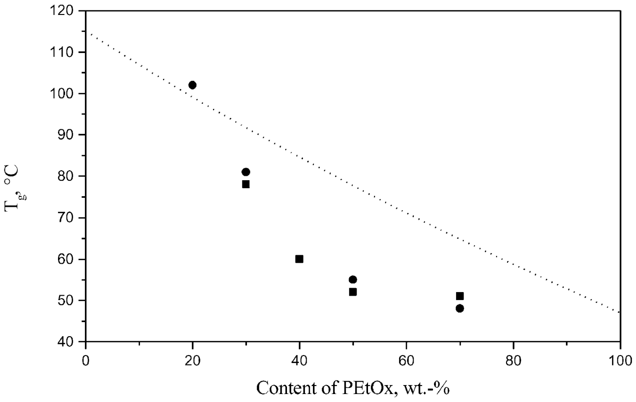


Fig. 2. Dependence of the glass transition temperatures of PEtOx–PMMA SPNs, measured by DSC, on the PEtOx weight fraction in the initial reaction mixture: PEtOx2500–PMMA (■) and PEtOx4300–PMMA (●) (networks obtained by thermal polymerization). The dotted line represents the values obtained with the Fox equation.

Such a DSC-behaviour could be regarded as an indication for the compatibility of the networks on a level of several tens of nanometres. On the other hand, the values corresponding to transitions in the DSC curves deviate much from the T_gs as predicted by the equation of Fox for miscible polymer blends [19], as can be observed in Fig. 2. Moreover, DMTA analyses of the same samples revealed phase-separated morphologies (Fig. 3) as demonstrated by the occurrence of two transitions.

The tan δ–T curve of the network PEtOx2500$_{40}$–PMMA (Fig. 3; curve A) exhibits a peak at 115 °C, associated with the PMMA-phase, and a shoulder at 80 °C which is assigned to a partially mixed PEtOx–PMMA phase. The loss peak of the network PEtOx2500$_{50}$–PMMA is split into two maxima, the temperatures of which are further shifted inwards compared to the transitions in curve A (Fig. 3; curve B). This indicates again that the networks with intermediate compositions show more compatible phase morphologies.

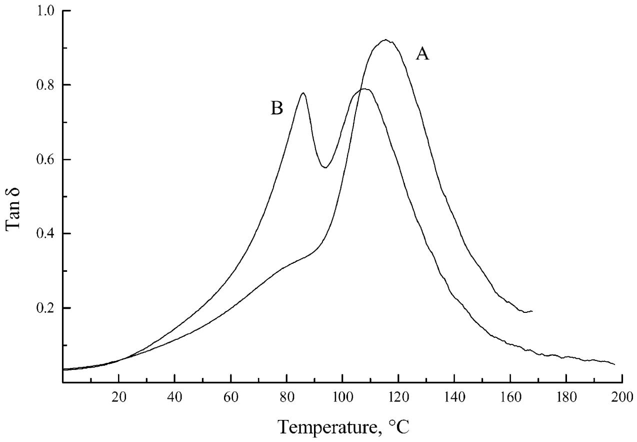


Fig. 3. tan δ versus temperature of (A) PEtOx2500$_{40}$–PMMA and (B) PEtOx2500$_{50}$–PMMA SPNs (obtained by thermal polymerization).

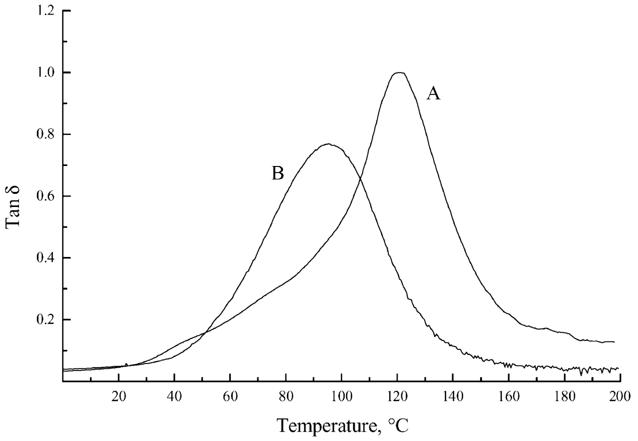


Fig. 4. tan δ versus temperature of (A) PEtOx4300$_{50}$–PMMA (obtained by thermal polymerization) and (B) PEtOx4300$_{50}$–PMMA (obtained by UV polymerization) SPNs.

In Fig. 4, the DMTAs of two samples containing the same content of PEtOx ($M_n = 4300$) and PMMA, but prepared with two different polymerization techniques, respectively, thermal (curve A) and UV initiation (curve B), are presented.

The DMTA of the network obtained by thermal polymerization shows a maximum in tan δ at 120 °C. This transition further extends to lower temperatures with a shoulder around 40 °C. This shows that the network has a phase-separated morphology. The network obtained by the UV technique shows a rather broad but single loss peak with one maximum at 96 °C, indicating a more compatible morphology. This difference could be ascribed to the difference in polymerization times and, correspondingly, in the kinetics of the gelation and phase separation process. In the case of UV initiation, the time of gelation is in the range of tens of seconds. Therefore, it can be assumed that the gelation process of these networks precedes the start of the phase separation process, leading to immobilized, non-equilibrium systems in which the driving force for phase separation is counterbalanced by the presence of cross-links. These data illustrate the influence of the polymerization conditions on the morphology of the final network.

3.3. Swelling behaviour

The influence of the copolymer composition on the equilibrium degree of solvent weight uptake for PMeOx-containing samples in water (good solvent for PMeOx and non-solvent for PMMA) and in acetone (solvent for PMMA and non-solvent for PMeOx) is presented in Fig. 5. As expected for these amphiphilic copolymers, the water uptake gradually increases with higher weight fraction of the hydrophilic component while the acetone uptake decreases. There is a composition at which the network swells equally in acetone and water. Such behaviour is

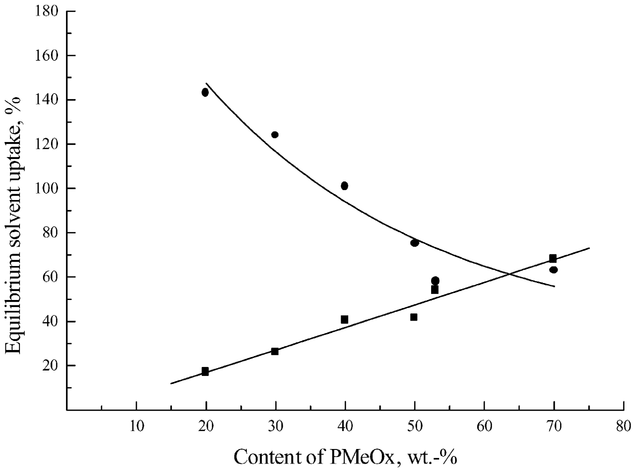


Fig. 5. Solvent uptake of PMeOx2800–PMMA SPNs in water (■) and acetone (•) as a function of PMeOx weight fraction in the initial reaction mixture.

typical for macromolecular substances containing segments of opposite philicity.

The equilibrium degree of solvent weight uptake for the PEtOx-containing networks in water also follows a gradual increase with the PEtOx content. As expected, the reversed situation is observed with toluene, which is a good solvent for PMMA and a non-solvent for PEtOx (Figs. 6 and 7). On the other hand, the swelling behaviour of PEtOx-containing copolymer networks in acetone is more complex and not only depends on the copolymer composition but also on the length of the polyoxazoline cross-links. Solubility experiments showed that acetone is a poor solvent for low molecular weight PEtOx but a good solvent for PEtOx with relatively high molecular weight. Therefore, networks with high molecular weight PEtOx segments as macromolecular cross-linker show a high degree of solvent uptake in acetone, almost independent of the copolymer composition (Fig. 7), while the acetone uptake of the samples with low molecular weight PEtOx segments decreases with increasing polyoxazoline content (Fig. 6).

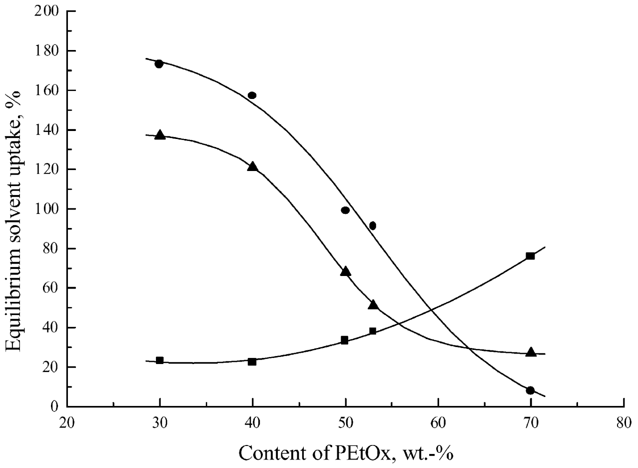


Fig. 6. Solvent uptake of PEtOx2500–PMMA SPNs in water (■), acetone (•) and toluene (▲) as a function of PEtOx weight fraction in the initial reaction mixture.

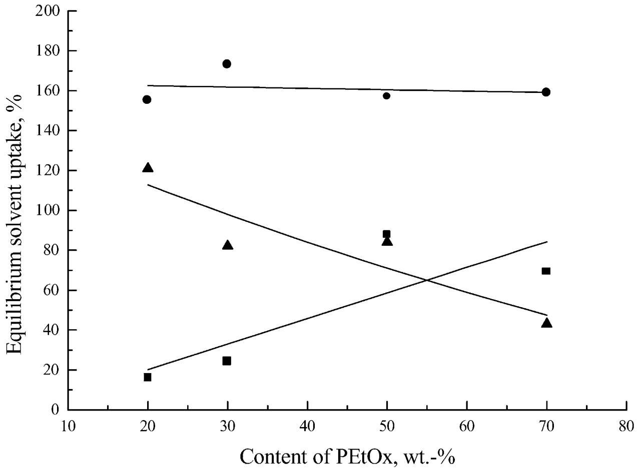


Fig. 7. Solvent uptake of PEtOx4300–PMMA SPNs in water (■), acetone (•) and toluene(▲) as a function of PEtOx weight fraction in the initial reaction mixture.

4. Conclusions

Polyoxazoline bis-macromonomers are useful building blocks in designing amphiphilic copolymer networks by using these reactive precursors as comonomers in the radical polymerization of MMA. Series of such networks were obtained in which hydrophilic PMeOx and PEtOx segments act as cross-links for hydrophobic PMMA chains. The hydrophilic–hydrophobic balance, the swelling and mechanical properties of the materials can be varied over a broad range by changing the nature, the molecular weight and the content of the polyoxazoline precursor in the networks. The phase morphology of the networks can be influenced by the synthetic conditions used for the construction of the segmented networks.

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