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Thermotropic Networks Based on Poly(Methyl Vinyl Ether)

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ABSTRACT

Segmented polymer networks consisting of poly(methyl vinyl ether) (PMVE) and a second polymer were synthesized by copolymerization of PMVE-α,ω-bis-methacrylate with a hydrophilic vinyl monomer (hydroxyethyl methacrylate, HEMA) or a hydrophobic vinyl monomer (styrene, St or butyl acrylate, BA). Such networks, swollen to equilibrium in water, show thermotropic properties in the case of the PMVE-PSt and PMVE-PBA systems due to the lower critical solution temperature (LCST) properties of the PMVE segments. The PMVE-PHEMA networks showed an inverse thermotropic behavior, i.e., the swollen networks are turbid at lower temperature and become transparent at higher temperature. The PMVE-PSt networks containing a small fraction of PSt are the best materials for thermotropic properties because the swelling is limited to a few percent which results in materials free of cracks after repeated heating–cooling (with corresponding de-swelling–swelling) processes.

Key Words: Polymer networks; Poly(methyl vinyl ether); LCSTL lower critical solution temperature; Thermotropic behavior; Segmented polymer networks.

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INTRODUCTION

Thermotropic materials can be applied to reflect sunlight above a given temperature ("cloud point temperature," T_c) and thereby act as an auto-regulating system for temperature control. The operating principle of a thermotropic layer, placed between two glass-plates, is demonstrated in Fig. 1. Such systems can be used for temperature auto-regulation in buildings with large glazed surfaces, green houses or as protection from strong sunlight in general.

A simple thermotropic system is obtained by filling the gap between two glass plates with a solution of a polymer showing a lower critical solution temperature (LCST) behavior.[1–3] An important drawback of this device is settling of the polymer particles after a certain time, which results in irreversibility of the system.[4] This problem can be overcome by addition of additives, which adjust the density of the solution to the density of the polymer solute or by increasing the viscosity.[5] An alternative solution is to crosslink the polymer, so that precipitation becomes impossible. Such gels, obtained from poly(N-isopropyl acrylamide)[6] and from other LCST-type polymers[7] have been described recently for application in thermotropic glazing. A disadvantage of using gels of crosslinked LCST-type polymers is their swelling/de-swelling behavior, caused by the temperature change, which may lead to the formation of cracks in the window glazing after a few temperature cycles.

Poly(methyl vinyl ether) (PMVE) is another polymer which exhibits an LCST-type behavior in water around 37°C.[8,9] In the present work, polymer networks containing PMVE segments were prepared and evaluated as thermotropic materials. Hydrogels obtained from pure PMVE networks show important swelling/de-swelling behavior which gave rise to crack-formation. It was investigated whether the swelling of the networks could be decreased by incorporating in the network a water-insoluble polymer segment or whether the de-swelling could be decreased by incorporation of a second water-soluble polymer segment, without loosing the thermotropic properties.

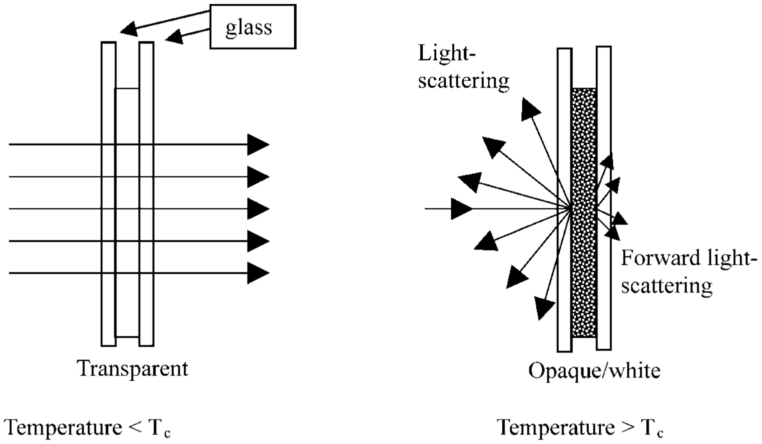

Figure 1. Operating principle of a thermotropic layer between two glass plates.

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RESULTS AND DISCUSSION

Synthesis of the PMVE-Based Segmented Networks

Segmented polymer networks were prepared by copolymerization of PMVE-α,ω-bis-methacrylate with a chosen co-monomer.

PMVE-bis-methacrylates with predictable molar mass can be produced by bifunctionally growing living cationic polymerization of MVE, followed by end-capping with 2-hydroxyethyl methacrylate (HEMA), as reported previously.[9,10] To obtain the segmented networks, the PMVE-bis-methacrylates were copolymerized with butyl acrylate (BA) or styrene (St) to introduce water-insoluble segments and with HEMA to introduce water-soluble segments (Fig. 2). In these segmented polymer networks, PMVE-chains are covalently bonded to polymer chains of the second monomer. In the present

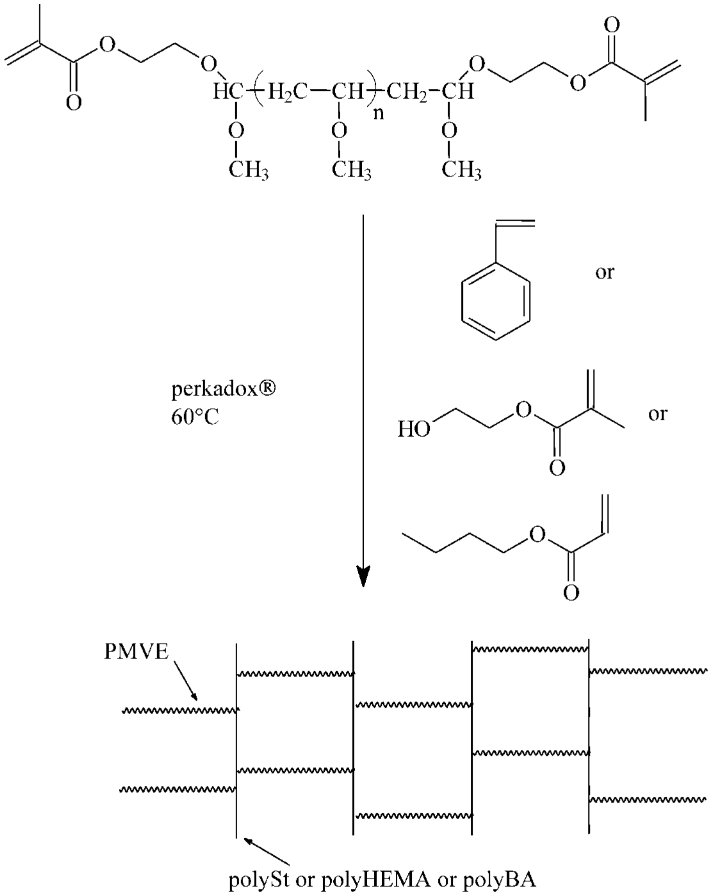

Figure 2. Synthesis of a segmented polymer network by copolymerization of PMVE-bis-methacrylate with a vinyl monomer.

work, PMVE-bis-methacrylates with M_n ranging from 1500 to 5000 g/mol and polydispersities of 1.1–1.2 were used. Segmented networks with various compositions were made by free radical initiated copolymerization in bulk (for high comonomer content), or as a concentrated solution (in toluene). Polymerizations were initiated with Perkadox®, and performed between two glass plates, separated by a spacer of 0.1 or 0.5 mm thickness, at 60°C for 10 hrs. The soluble fractions of the networks were always lower than 10%.

Characterization of the Networks

The PMVE-BA and PMVE-St networks, in dry form, are transparent materials, suggesting that there is no phase separation between the polymer segments. This was confirmed by dynamic mechanical thermal analysis (DMTA) measurements which showed only one maximum in the tanδ-temperature curves, as shown in Fig. 3. PMVE-PHEMA-networks, on the contrary, are opaque materials which show two maxima in their tan δ-temperature curves (Fig. 4), proving that under the used polymerization conditions, phase separation has taken place.

The swelling properties in water are, as discussed in the introduction, important for the applicability of the polymer networks as thermotropic glazing materials. Table 1 gives an overview of swelling degrees of different networks with different compositions. It can be seen that PMVE-PBA systems with high PMVE content show a high degree of swelling at room temperature but that above the LCST, de-swelling is almost complete.

In the PMVE-PHEMA systems, the swelling is high at low temperature. Above the LCST, de-swelling takes place but the end product still contains a high fraction of water

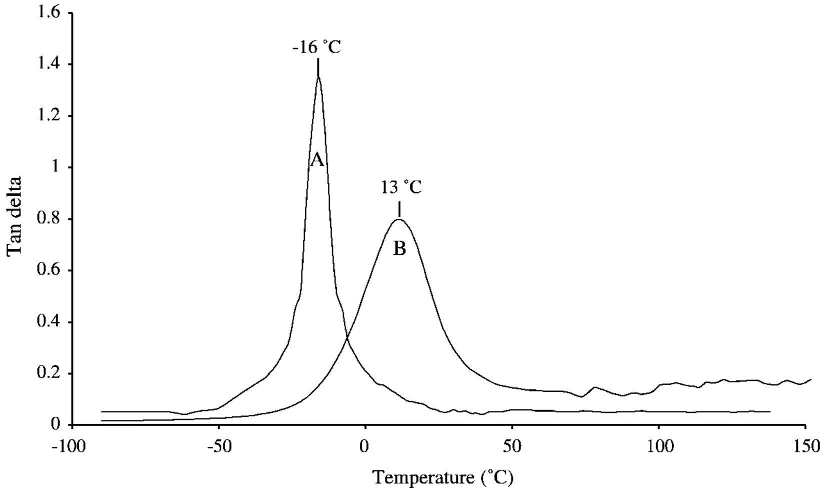

Figure 3. Dynamic mechanical thermal analysis of (60/40 wt%)PMVE-PBA (A) and (60/40 wt%)PMVE-PSt (B).

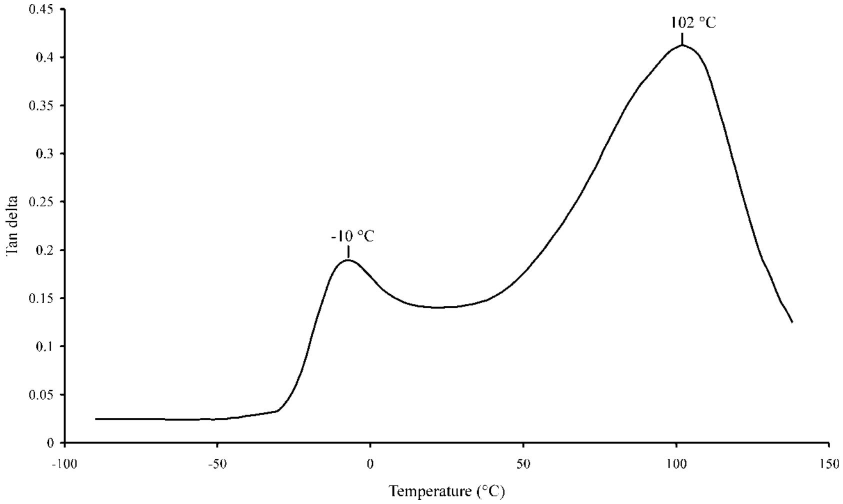

Figure 4. Dynamic mechanical thermal analysis of (60/40 wt%)PMVE-PHEMA.

due to the presence of the hydrophilic PHEMA domains. The PMVE-PSt systems seem the most promising because the swelling is very limited even with small fractions of PSt.

Thermotropic Properties of the PMVE-Based Networks

The thermotropic properties of the PMVE-based films (thickness 0.1 mm) were evaluated by measuring the transmission of light (wavelength 520 nm) through the films,

Table 1. Equilibrium degree of swelling[a] in water for different PMVE-containing segmented polymer networks at 20 and at 40°C.

Comonomer	Wt% PMVE in network	M_n(PMVE)[b]	Degree of swelling at 20°C (%)	Degree of swelling at 40°C (%)
HEMA	2	4900	64	54
HEMA	25	4900	87	53
HEMA	60	3000	100	39
St	60	4100	2	0
St	90	4100	4	0
St	95	4100	14	1
BA	90	4100	90	<10
BA	95	4100	140	<10

[a] Expressed as $100(w_s - w_o)/w_o$ with w_o: weight of dry network and w_s: weight of swollen network.
[b] Number average molar mass of PMVE-bis-methacrylate used for network preparation.

swollen in water to equilibrium and put between two glass plates, as a function of temperature (compared to the transmission of light through a 1 cm cell filled with water).

PMVE-PSt Networks

The thermotropic behavior of the PMVE-PSt networks containing 5, 10, and 20 wt% of PSt, is illustrated in Fig. 5. When the St-content in the networks is higher than 20 wt%, the swollen materials are opaque at room temperature and therefore are not suitable for glazing applications. From Fig. 5, it can be seen that the cloud point temperature decreases with increasing St-content in the networks. It is also clear that the networks containing 5 or 10% of St, are transparent at 25°C and become almost completely reflective above the cloud point temperature. Fig. 6 illustrates the thermotropic behavior of this material. Because these materials show a low swelling degree in water at room temperature (15% and 4% swelling at 20°C for 5 and 10 wt% of St, respectively), they are the best thermotropic materials obtained in this study.

Poly(MVE-co-BA)

Water-swollen PMVE-PBA networks with a low BA content are transparent enough at room temperature to be used as thermotropic materials. Fig. 7 shows that the cloud point temperature decreases with increasing BA-content in the networks. The transition from

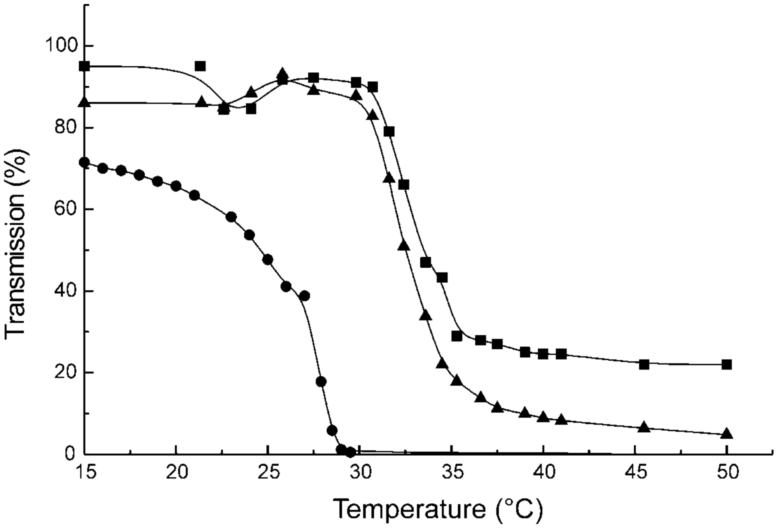

Figure 5. Transmission of light (520 nm) through PMVE-PSt films with different compositions (and swollen to equilibrium in water at 20°C) as a function of temperature (dry film thickness: 100 μm, 5 wt% PSt (■); 10 wt% PSt (▲); 20 wt% PSt (•)).

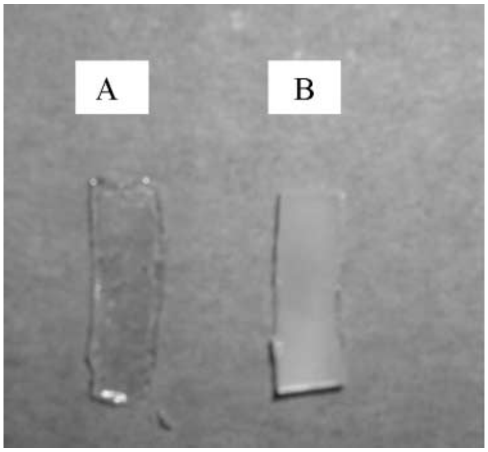

Figure 6. Photographs illustrating the thermotropic effect of a (90/10 wt%) PMVE-PSt network (A: 20°C and B: 40°C).

transparent to opaque for these networks is more continuous than for PMVE-PSt networks. The PMVE-PBA networks with 10 and 5% of BA have an equilibrium swelling degree in water at 20°C of 85 and 140%, which is too high for practical applications. Maybe this problem could be overcome by increasing the crosslink density of the networks by addition of a low molecular crosslinking agent during the network formation.

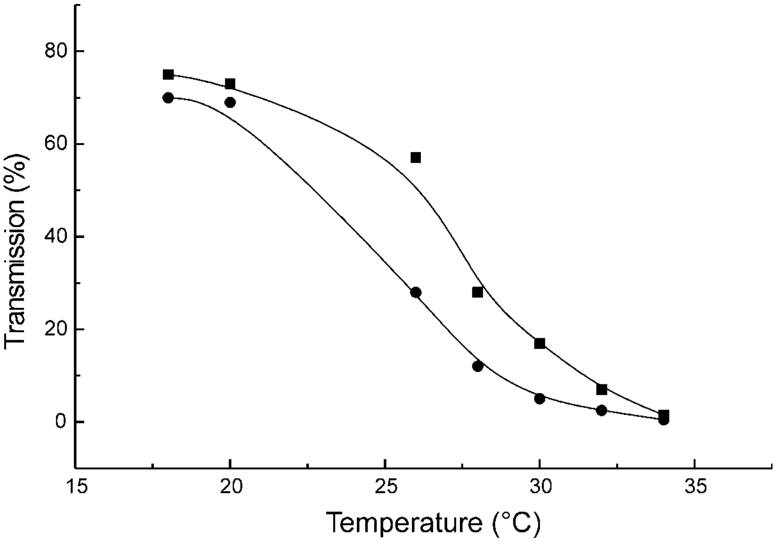

Figure 7. Transmission of light (520 nm) through PMVE-PBA films with different compositions as a function of temperature (film thickness: 100 μm, 5 wt% PBA (■); 10 wt% PBA (•)).

PMVE-PHEMA Networks

The networks with a PMVE content lower than 40% do not show a thermotropic effect at all: they are non-transparent at all temperatures. Remarkable is that the PMVE-PHEMA networks with a PMVE content between 40 and 60% show an inverse thermotropic effect: the gels are opaque at room temperature and become transparent when the temperature is increased. This inverse thermotropic effect is demonstrated in Figs. 8 and 9. The maximum in transparency depends on the composition: an increasing PMVE content results in higher transparency. The inverse thermotropic effect indicates a complicated phase behavior of the system PMVE/PHEMA/H_2O as a function of temperature.

EXPERIMENTAL

Materials

The PMVE-bis-methacrylates were prepared as reported earlier.[9,10] 2-Hydroxyethyl methacrylate (HEMA; Fluka) was purified by a five-fold extraction of 50 ml of HEMA dissolved in 5 ml of water with 100 ml of cyclohexane to remove residual ethylene glycol dimethacrylate. Residual methacrylic acid was separated from HEMA by saturation of the water phase with sodium chloride and extraction with diethyl ether. The ether phase was dried over $MgSO_4$ and diethyl ether was removed in a rota-vaporator. HEMA was distilled

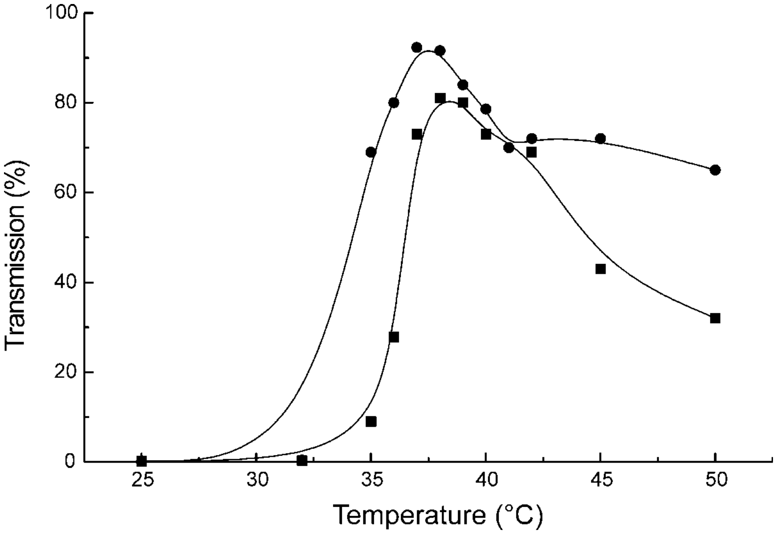

Figure 8. Transmission of light (520 nm) through PMVE-PHEMA films with different compositions as a function of temperature (film thickness: 100 μm, 60 wt% PHEMA (•); 40 wt% PHEMA (■)).

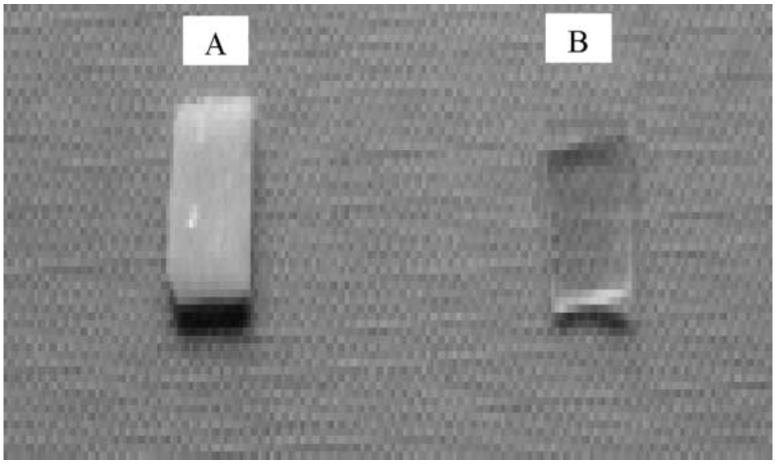

Figure 9. Photograph illustrating the inverse thermotropic effect of a (60/40 wt%) PMVE-PHEMA network (A: 20°C and B: 37°C).

in the presence of t-butyl catechol as inhibitor. Butyl acrylate (BA; Fluka), styrene (St., Aldrich) and toluene (HPLC grade) were used as received.

Preparation of Segmented Networks Based on PMVE-bis-Methacrylate

The networks were prepared by dissolving 0.15 g of styrene and 2.85 g of PMVE-bis-methacrylate ($M_n = 4100$ g/mol) in 1 ml of toluene. 32 mg of Perkadox® was added and the mixture was degassed four times. The mixture was injected between two glass plates separated by a silicon spacer (thickness 0.1 mm) and heated to 60°C for 10 h. The networks were removed from the glass plates and ‘post-cured’ in a vacuum oven at 80°C for 12 hrs.

Cloud Point Measurements

The cloud point curves were measured with a Kontron UVIKON 810 spectrophotometer in transmission mode at a fixed wavelength of 520 nm.

Swelling Measurements

A piece of dried and weighed network was immersed in water at roomtemperature and then weighed periodically until constant weight was reached. The equilibrium degree of swelling (Q) was expressed as $Q = 100\left(\frac{w_s - w_o}{w_o}\right)$, where w_o and w_s, denote the weight of a sample before and after swelling.

DMTA Measurements

Were obtained with a TA instrument Type PL-DMTA MkII using a frequency of 1 Hz and a heating rate of 5°C/min.

CONCLUSION

It was shown that water-swollen segmented networks composed of PMVE and relatively small fractions of a hydrophobic polymer such as PSt or PBA, show thermotropic behavior, i.e., these materials are transparent at room temperature and become reflective above the cloud point situated between 30 and 35°C. The PMVE-PSt-networks with low PSt fractions (5–10%), have a low degree of swelling which results in stable gels which withstand several swelling/de-swelling procedures without the appearance of cracks. Water-swollen PMVE-PHEMA networks show an inverse thermotropic behavior, i.e., the materials are reflective at room temperature and become transparent above the LCST of PMVE.

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