

Thermodynamic Analysis of the Reaction-Induced Phase Separation of Solutions of Random Copolymers of Methyl Methacrylate and *N,N*-Dimethylacrylamide in the Precursors of a Polythiourethane Network

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ABSTRACT: Poly(methyl methacrylate) and random copolymers of methyl methacrylate (MMA) and *N,N*-dimethylacrylamide (DMA) containing 7.5, 15, or 20 wt % DMA were dissolved in a stoichiometric mixture of *m*-xylylene diisocyanate and 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol, precursors of a polythiourethane network. Phase separation, which took place during polymerizations at 60, 90, and 120 °C, exhibited a lower critical solution temperature behavior. The cloud-point conversions, which were determined by the iodometric titration of free thiol groups of samples chilled in ice at the cloud point, increased with the weight fraction of DMA in the random copolymer. This could be used to control the cloud-point conversion and determine the characteristic size of the dispersed domains. A thermodynamic analysis was performed with the Flory–Huggins equation, taking into account the polydispersities of both the thermoplastic and thermoset polymers and using an interaction parameter depending on the temperature and on the three binary interaction energies. A reasonable fitting of the experimental curves was obtained with negative values for the interaction energies of the MMA–thermoset and DMA–thermoset pairs and with a positive value for the MMA–DMA pair. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 44: 2821–2827, 2006

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INTRODUCTION

Transparent polymers have found increasing applications as optical materials because of their lower densities and better mechanical properties and processability in comparison with inorganic

glasses. To make eyeglass lenses, it is convenient to use materials exhibiting high refractive indices to reduce their thicknesses. Sulfur-containing polymers such as polythiourethanes (PTUs) exhibit high refractive indices and are excellent candidates for optical materials.^{1–3} However, other properties, such as the fracture resistance, should also reach the required values. The fracture resistance of a transparent material can be increased by the production of a fine dispersion of domains of a rubbery or thermoplastic phase

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with characteristic sizes much lower than the range of wavelengths of visible light.^{4–7}

The toughening of a PTU network requires the selection of a convenient modifier and an effective way of controlling the characteristic size of the dispersion generated. A simple way of controlling this size is polymerization-induced phase separation.^{8,9} In this process, the starting point is a homogeneous solution of the modifier in the PTU precursors (e.g., a stoichiometric solution of a trithiol and a diisocyanate). In the course of polymerization, a phase separation is produced, mainly due to the increase in the average size of the thermoset species and the corresponding decrease in the entropic contribution to the free energy of mixing.⁸ The cloud-point conversion depends on the binary interaction energy between the thermosetting polymer and the modifier. Reducing the interaction energy shifts the cloud-point conversion to higher values (more miscible modifiers phase-separate at higher conversions). At a particular polymerization temperature, an increase in the cloud-point conversion produces phase separation in a more viscous medium and a significant reduction in the characteristic size of the dispersed domains. A very low value of the cloud-point conversion can lead to macrophase separation. In an intermediate conversion range located well before the gel conversion, typical microphase separation is produced. When phase separation takes place close to the gel conversion or in the postgel stage, the size of the dispersed domains is usually in the nanometer range.⁴

The problem is to select a convenient modifier that can exhibit variable miscibility with the PTU precursors depending on its chemical structure. For conventional epoxies, this is achieved with random copolymers of acrylonitrile (miscible block) and butadiene (immiscible block). Increasing the acrylonitrile fraction in the random copolymer leads to a shift of the cloud-point conversion to higher values, a factor that is used in practice to match the initial miscibility and the cloud-point conversion.^{8,10} A similar approach was investigated in this study. Preliminary tests showed that poly(methyl methacrylate) (PMMA) was initially miscible in the PTU precursors and that phase separation occurred at intermediate conversions in the course of polymerization. On the other hand, a very polar polymer such as poly(*N,N*-dimethylacrylamide) was soluble up to the complete conversion. Therefore, random copolymers of both monomers were convenient choices to vary the cloud-point conversion with the copolymer composition.

The aim of this article is to analyze the polymerization-induced phase separation of random copolymers of methyl methacrylate (MMA) and *N,N*-dimethylacrylamide (DMA) dissolved in the precursors of a PTU network. Emphasis is placed on a thermodynamic analysis of the miscibility during polymerization, which considers the binary interaction energies between the different constitutional units: MMA–thermoset, DMA–thermoset, and MMA–DMA. The characterization of the monomers and the determination of the structural transitions and final properties of the neat PTU network have been published elsewhere.¹¹ A discussion of the morphologies and properties generated in PTU networks modified by random copolymers of MMA and DMA will be the subject of a subsequent publication.

EXPERIMENTAL

Materials

The trithiol was 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [density (ρ) = 1.27 g/cm³], and the diisocyanate was *m*-xylylene diisocyanate (ρ = 1.21 g/cm³); both were provided by Mitsui Chemicals (Fig. 1). They were used in stoichiometric proportions and polymerized at 120 °C without any catalyst and at 60 and 90 °C with 0.01 wt % dibutyltin dichloride as the catalyst.¹¹ The gel conversion was close to 0.70, in agreement with the value expected for an ideal stepwise polymerization of a stoichiometric mixture of a bifunctional monomer and a trifunctional monomer [ideal value of the gel conversion (p_{gel}) = 0.707].¹¹

PMMA [number-average molecular weight (M_n) = 10,600, weight-average molecular weight (M_w) = 15,100, ρ = 1.16 g/cm³] was provided by Aldrich. The poly(methyl methacrylate-*co-N,N*-dimethylacrylamide) random copolymers (Fig. 1) were synthesized by nitroxide-mediated radical polymerization by the group of Professor D. Bertin (Unité Mixte de Recherche 6517, Université d'Aix-Marseille, France). Three different products were used with DMA fractions equal to 7.5 wt % (M_n = 27,300, M_w = 36,100, ρ = 1.15 g/cm³), 15 wt % (M_n = 25,700, M_w = 34,400, ρ = 1.14 g/cm³), and 20 wt % (M_n = 30,100, M_w = 40,100, ρ = 1.13 g/cm³).

Size Exclusion Chromatography

Average molar masses and molar mass distributions of the different thermoplastic modifiers

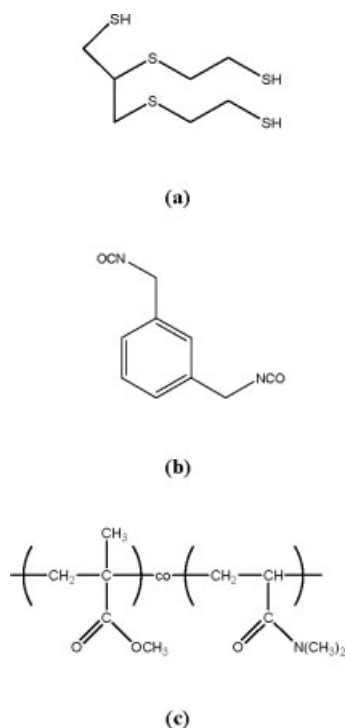


Figure 1. Chemical structures of (a) the trithiol, (b) the diisocyanate, and (c) the random copolymer.

were determined by size exclusion chromatography with a Waters device equipped with a 6000A pump, a U6k-type injector, and three columns with PSS SDV gel (5×10^4 , 10^3 , and 10^2 Å). Tetrahydrofuran was used as the solvent at a flow rate of 1 mL/min at 35 °C. A Viscotek VE3580 differential refractive-index detector and a Dual T60 light scattering detector combined with a viscometer were used. PMMA standards were employed to characterize the commercial PMMA, and double detection was used to characterize the random copolymers. The dn/dc values (derivative of the refractive index with respect to concentration) were determined with the refractive-index detector, and the average molar masses were determined with the light scattering detector.

Cloud-Point Conversions

Solutions of the different thermoplastics in the thermoset precursors were homogeneous at the start of the polymerization. The reaction was carried out in a test tube kept at the desired temperature (60, 90, or 120 °C) inside a light transmission device. The cloud point was arbitrarily defined as the particular time at which the intensity of visible light transmitted through the

sample began to decrease because of the presence of an emergent phase. This required that the characteristic size of the emergent phase attain a value close to about 100 nm to scatter visible light.⁸ As the polymerization rate was relatively slow under the selected reaction conditions (e.g., 96 min to attain the gel point at 120 °C),¹¹ the advance in conversion during the time that elapsed for the generated phase to attain the critical size was considered negligible.

At the cloud point, the tube was taken out of the light transmission device and chilled in ice. The cloud-point conversion was determined by the iodometric titration of residual thiol groups.¹¹

RESULTS AND DISCUSSION

The phase separation of PMMA in the course of polymerization was first investigated. Figure 2 shows experimental values of the cloud-point conversions for polymerizations carried out at 60, 90, and 120 °C. Increasing the temperature produced a decrease in the cloud-point conversion, which supported lower critical solution temperature (LCST) behavior. This can be explained by the presence of specific interactions (hydrogen bonds) between the thermoplastic and the thermosetting polymer. The strength of these bonds decreases with an increase in temperature and renders the blend less miscible.

The random copolymer containing 7.5 wt % DMA exhibited similar LCST behavior (Fig. 3). For the same polymerization temperature, phase separation occurred at higher conversions than in the case of PMMA, indicating an increase in

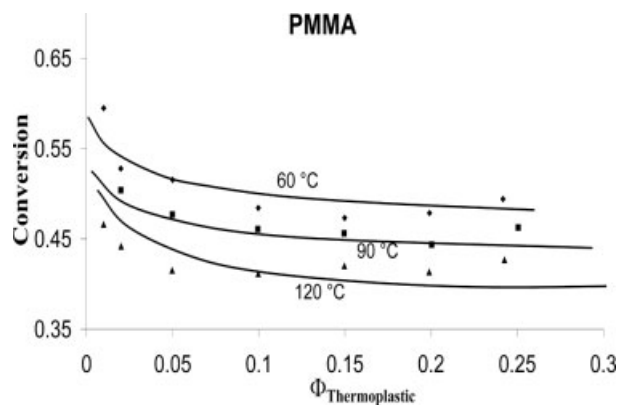


Figure 2. Cloud-point conversion as a function of the volume fraction of PMMA at three polymerization temperatures.

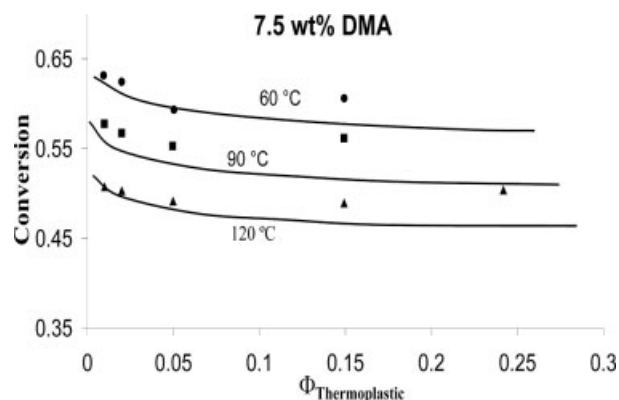


Figure 3. Cloud-point conversion as a function of the volume fraction of the random copolymer containing 7.5 wt % DMA at three polymerization temperatures.

the miscibility produced by DMA. The effect of the amount of DMA in the random copolymer on the cloud-point conversions is shown in Figures 4–6 at three different polymerization temperatures. At 60 °C, only 7.5 wt % DMA was necessary to drive cloud-point conversions to values close to gelation ($p_{gel} = 0.70$). At 120 °C, this level of cloud-point conversion required 20 wt % DMA in the random copolymer as a result of the LCST behavior.

The Flory–Huggins model was used to fit the experimental curves. The free energy per mole of unit cells with molar volume V_r can be written as follows:

$$\Delta G/RT = \sum \sum (\phi_{m,n}/r_{m,n}) \ln \phi_{m,n} + \sum (\phi_{2i}/r_{2i}) \ln \phi_{2i} + \chi \phi_1 \phi_2 \quad (1)$$

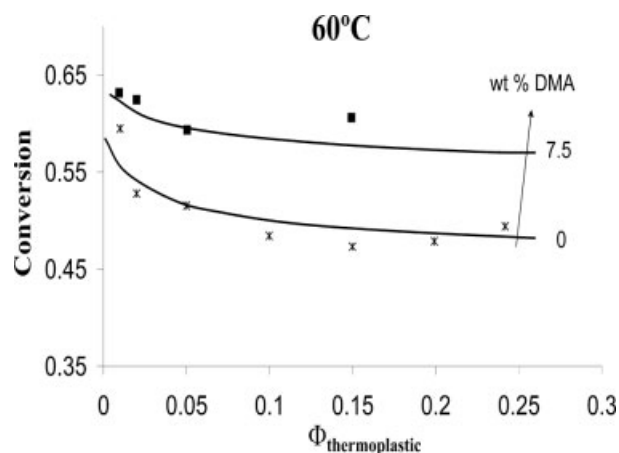


Figure 4. Cloud-point conversion as a function of the volume fraction of random copolymers containing different weight percentages of DMA at 60 °C.

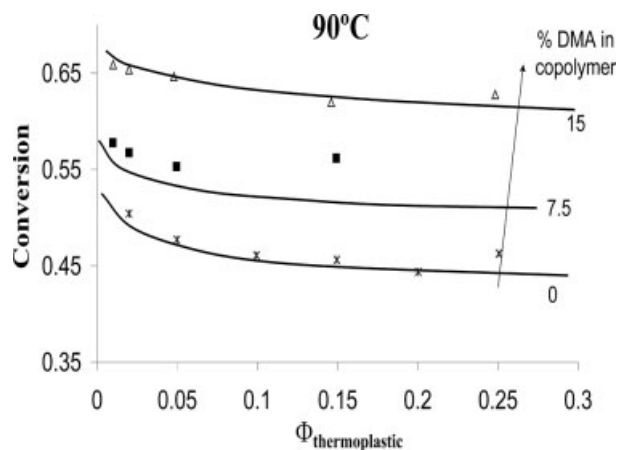


Figure 5. Cloud-point conversion as a function of the volume fraction of random copolymers containing different weight percentages of DMA at 90 °C.

where ΔG is the free energy per mole of unit cells, R is the gas constant, T is the temperature, $\phi_{m,n}$ represents the volume fraction of species of the thermosetting polymer with m units of the diisocyanate and n units of the trithiol ($\sum \phi_{m,n} = \phi_1$), $r_{m,n}$ is the size measured with respect to reference volume V_r [taken as the molar volume of MMA ($86.207 \text{ cm}^3/\text{mol}$)], ϕ_{2i} represents the volume fraction of the i -mer of the thermoplastic ($\sum \phi_{2i} = \phi_2$), r_{2i} is the size of the i -mer measured with respect to the reference volume, and χ is the interaction parameter.

The distribution of species of the thermoplastic was obtained from the average values of molar masses under the assumption of a Schulz–Zimm distribution.⁹ The distribution of species of the thermosetting polymer at any conversion (p)

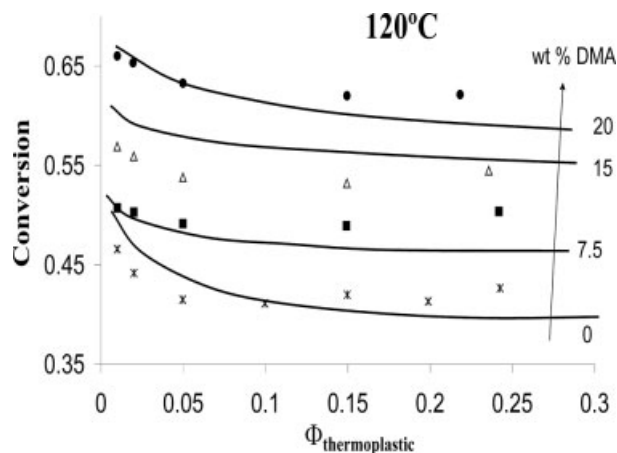


Figure 6. Cloud-point conversion as a function of the volume fraction of random copolymers containing different weight percentages of DMA at 120 °C.

was obtained under the assumption of an ideal stepwise polymerization:¹²

$$N_{m,n} = 2I_0(2n)!p^{m+n-1}(1-p)^{2+n} / [(m-n+1)!(2n-m+1)!n!] \quad (2)$$

where $N_{m,n}$ is the molar concentration of a generic species containing m diisocyanate units and n trithiol units and I_0 is the initial molar concentration of the diisocyanate in the stoichiometric mixture (calculated under the assumption that there was no volume variation upon mixing).

The presence of factorials in eq 2 leads to numerical problems for large values of n and m (e.g., when Mathcad is used to obtain the distribution, the maximum factorial that can be used is 170!; this would limit the calculation to a maximum n value of 85 which is not enough to simulate distributions in the vicinity of the gel conversion). To solve this numerical problem, a recursive algorithm was generated with the following definitions:

$$N_{m,n} = 2I_0 f_{m,n} \quad (3)$$

The factor $f_{m,n}$ is calculated in an inductive way:

$$f_{0,0} = (1-p)^2/p \quad (4)$$

$$f_{1,0} = (1-p)^2/2 \quad (5)$$

$$f_{n-1,n} = f_{n-1,n-1} 2(1-p)p(2n-1)/[(n+1)(n+2)] \quad (6)$$

$$f_{m,n} = f_{m-1,n} p(2n-m+2)/(m-n+1); \quad n \leq m \leq 2n+1 \quad (7)$$

The factor $f_{0,0}$ that is needed in the recursive procedure has no physical meaning (as well as $N_{0,0}$). Monomers are represented by $N_{1,0}$ (diisocyanate) and $N_{0,1}$ (trithiol). The size of the generic species, $r_{m,n}$, was calculated by the division of the volume of the species (under the assumption of no contraction upon polymerization) by the reference volume. The volume fraction of the generic species is given by

$$\phi_{m,n} = (N_{m,n}r_{m,n}/\sum\sum N_{m,n}r_{m,n})\phi_1 \quad (8)$$

Distributions were truncated, including a number of species necessary to obtain the experimental value of M_w for the thermoplastic and the ideal theoretical value for the thermosetting polymer,¹² with a deviation less than 0.1%.

χ was taken as a typical function of temperature:

$$\chi = a + b/T \quad (9)$$

where factor b , which incorporates the total number of binary interactions, should be a negative value to simulate the experimental LCST behavior. For the particular case of the interactions among the units of a random copolymer (MMA and DMA) and a solvent (PTU), b is given by¹³

$$b = (V_r/R)[B_{\text{MMA-PTU}} + (B_{\text{DMA-PTU}} - B_{\text{MMA-PTU}} - B_{\text{MMA-DMA}})\phi_{\text{DMA}} + B_{\text{MMA-DMA}}\phi_{\text{DMA}}^2] \quad (10)$$

where ϕ_{DMA} is the volume fraction of DMA in the random copolymer and B_{ij} is the interaction energy per unit of volume of the couple i - j . An implicit assumption of eq 10 is that the quality of the solvent (PTU) is the same in the conversion range of the experimental cloud-point conversions ($p = 0.35$ – 0.65). A general observation for the case of polymerization-induced phase separation in other thermosetting polymers (mainly epoxies) is that the interaction parameter varies with the conversion.⁸ However, the variation is more significant at the beginning of the polymerization than at intermediate conversions.¹⁴ Therefore, the assumption of χ being independent of the conversion is considered reasonable in the conversion range covered by the experimental results.

Chemical potentials for both components [(1) the thermoset and (2) the thermoplastic] were derived from eq 1 with standard procedures.¹⁵ Equating them in both phases led to a couple of algebraic equations written in terms of two separation factors that relate the concentrations of every species in the initial and emergent phases.¹⁵ Both separation factors are related by a third equation stating that the summation of volume fractions of all species in the emergent phase equals 1. Therefore, the final system consists of three algebraic equations in three unknowns: two separation factors and the interaction parameter. These equations were solved for every experimental point with Mathcad 2001 Professional. This led to a series of values of the interaction parameter for different temperatures, initial compositions, and particular random copolymers.

First, the values obtained for PMMA were correlated, and this led to $B_{\text{MMA-PTU}} = -5.5 \text{ J/cm}^3$ and $a = 0.25$. The negative value obtained for the

Table 1. Binary Interaction Energies Taken from the Literature (Ref. 13) and Obtained in This Study (Binary Pair MMA/DMA) and Differences between the Solubility Parameters Calculated with the Fedors Group Contribution Method

Pair	$B_{\text{MMA},j}$ (J/cm^3)	$(\delta_j - \delta_{\text{MMA}})$ ($\text{J}^{1/2}/\text{cm}^{3/2}$)
MMA/maleic anhydride	30.0	16.3
MMA/acrylonitrile	18.1	9.5
MMA/DMA	11.6	4.9
MMA/ <i>t</i> -butyl methacrylate	5.7	-1.7
MMA/cyclohexyl methacrylate	3.3	-0.2
MMA/ <i>n</i> -butyl acrylate	1.9	-0.3
MMA/phenyl methacrylate	1.0	2.3
MMA/methyl acrylate	0.8	1.3
MMA/ethyl acrylate	0.5	0.6

interaction parameter is explained by hydrogen bonds between SH (reactant) or NH (reaction product) groups of the thermosetting polymer and the carbonyl groups of the MMA repeating unit. This is consistent with the observed LCST behavior. The values of the interaction parameters obtained for blends of random copolymers in the thermosetting polymer were correlated to fit the corresponding binary interaction energies with eqs 9 and 10. The resulting values were $B_{\text{DMA-PTU}} = -9.6 \text{ J}/\text{cm}^3$ and $B_{\text{MMA-DMA}} = +11.6 \text{ J}/\text{cm}^3$. The continuous curves shown in Figures 2–6 correspond to the fitting obtained with these values of the binary interaction energies.

However, because the range of copolymer compositions that could be explored was rather narrow, there was a correlation between the values of $B_{\text{DMA-PTU}}$ and $B_{\text{MMA-DMA}}$. This means that other fittings with a more negative value of $B_{\text{DMA-PTU}}$ coupled with a less positive value of $B_{\text{MMA-DMA}}$ were also (slightly less) reasonable.

The relatively high negative value observed for $B_{\text{DMA-PTU}}$ can be explained by the strong hydrogen bonds between the constitutional repeating units of both components. The high solubility of random copolymers containing DMA is explained by both the high negative value of the interaction energy of DMA with PTU and the repulsion between DMA and MMA units. The latter favors the miscibility of the random copolymer as it decreases the value of the resulting interaction parameter.¹³

The value obtained for the interaction energy between MMA and DMA lies in the same range

of values reported for the interaction energy of MMA with other constitutional repeating units,¹³ as shown in Table 1. The difference in the solubility parameters between the two units, as calculated with the Fedors group contribution method,¹⁶ is also shown in Table 1. Although there is some dispersion, it may be stated that high values of the interaction energy are associated with significant differences between the solubility parameters of both units. The value obtained in this article for MMA/DMA is consistent with the observed trend.

CONCLUSIONS

Random copolymers containing MMA and DMA units are initially miscible in the precursors of a PTU network but phase-separate in the course of polymerization. The phase diagram exhibits an LCST behavior indicating that miscibility increases when the temperature decreases. This is the result of specific interactions (hydrogen bonds) between the PTU and both units present in the random copolymer. Increasing the DMA weight fraction in the copolymer leads to a significant increase in the miscibility and may be used in practice to determine the cloud-point conversion and the characteristic size of the dispersed phase.

A thermodynamic simulation based on the Flory–Huggins model written in terms of binary interaction energies provided a reasonable fit with the experimental cloud-point curves. The interaction energies between MMA and DMA with the thermosetting polymer were both negative with a larger absolute value for DMA. This evidences the presence of specific interactions between both components that contribute to their miscibility. The interaction energy between MMA and DMA was positive with a value consistent with a set of values reported in the literature for pairs of MMA with a second component.

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