

Influence of the Process on Phase Separation Induced by Radical Copolymerization of Styrene and Divinylbenzene in the Presence of Reactive Polyurethane Network Precursors

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ABSTRACT: Interpenetrating polymer systems based on crosslinked polyurethane (PU) and polystyrene (PS) were prepared at room temperature by a one-shot (*in situ*) method, starting from an initial homogeneous mixture of reagents via noninterfering mechanisms. Both polymerizations were performed either simultaneously or one after the other. True simultaneity at every stages of the process is not possible. Despite the difference in refractive index of the components, hazy or optically clear films were obtained, thus indicating various levels of phase separation, also confirmed by glass transition temperature (T_g) measurements.

The results suggest that controlling the chemistry and process (crosslink density, composition, and time sequence of events) of *in situ* interpenetrating network formation will give various morphologies, and hence properties, ranging from microphase separated materials to larger macrophase separated materials. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2989–2996, 2006

Key words: interpenetrating networks (IPN); polyurethane; polystyrene; phase separation; glass transition

INTRODUCTION

In recent years, polymer mixing has continued to be a subject of intensive investigation in both technological and academic domains to obtain new materials. Interpenetrating polymer networks, IPNs, are one of the fastest growing fields in multicomponent polymeric materials because they exhibit special properties that result from crosslinking and interlocking of the polymer chains.¹ The morphology of IPNs is particularly complex as it is kinetically controlled in the case of a one-shot synthesis (simultaneous IPNs), starting from an homogeneous mixture of the components. In fact, the term simultaneous IPN is not appropriate as usually no information about the occurrence of deciding events such as formation of network I, formation of network II, phase separation, which all induce the final morphology is available. True simultaneity seldom occurs. For a better understanding of the development of morphology in IPN formation, we have prepared simultaneous IPNs, better named *in situ* IPNs,² by variation of the process: starting from the same initial homogeneous mixture of the component

precursors, *in situ* seq (sequential) IPNs were obtained by forming a first network followed by the polymerization and the formation of the second network. *In situ* sim (simultaneous) IPNs³ were made by performing both (noninterfering) reactions simultaneously, under kinetical control. The *in situ* IPNs under investigation here are based on polyurethane (PU) and polystyrene (PS), which are two highly incompatible polymers.

EXPERIMENTAL

Materials

Poly(oxypropylene glycol)s with molecular weights of approximately 1000 g/mol (Arcol® 1010), 2000 g/mol (Arcol® 1020), and 4000 g/mol (Arcol® 1025) were obtained from Arco Chemical Co. Hexamethylene diisocyanate isocyanurate (Desmodur® N3300) was kindly supplied by Bayer. Dibutyltin dilaurate (Kosmos® 19, Goldschmidt AG) was used as the catalyst for the reaction of macrodiol with triisocyanate. These reagents were used as received. Styrene (Merck) and divinylbenzene (DVB, 65% purity, Merck) were dried over molecular sieves, but not freed from their stabilizer. The free-radical initiators used in this work were either 2,2'-azobisisobutyronitrile (AIBN, Merck) or

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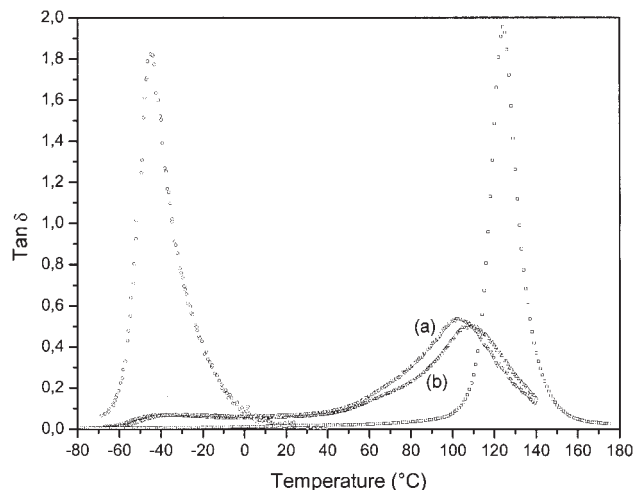


Figure 1 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* seq 35/65 PU/PS IPNs as a function of the free radical initiator and process: (a) benzoin at 25°C and (b) AIBN at 60°C. (○) individual networks. PU is based on Arcol 1020 (2000 g/mol).

2-hydroxy-2-phenylacetophenone (benzoin, Aldrich). They were used without further purification.

Preparation of *in situ* PU/PS IPNs

The *in situ* PU/PS IPNs were prepared at room temperature by a one-shot process. Under vigorous stirring, a proper amount of Arcol®, Desmodur®, styrene, DVB, and initiator was mixed for 5 min to form a homogeneous mixture. The ratio between isocyanate groups and hydroxy groups was 1.07, according to Tabka et al.⁴ The amount of crosslinking agent (DVB) was 5% by weight of styrene, and the amount of initiator (usually benzoin) was 0.5% by weight of vinyl monomers. Then, the catalyst (1.5% by weight based on the PU components) was added under stirring, and the mixture poured into a mold formed by two glass plates separated by an appropriate spacer and

clamped together. Entrapped air bubbles were removed under vacuum. To prepare *in situ* seq IPNs, the mold was kept at 25°C and placed in the dark for 24 h to allow complete formation of the PU network. Then, the mold was transferred in a thermostated (25°C) box, and exposed to the ultraviolet radiations (predominantly 365 nm) of a 100 W mercury lamp (UVP, Upland, CA). Light intensity at the surface was 7 mW cm⁻². After a given time, the polymerization was stopped, and the sample was removed from the mold. Unreacted chemicals (less than 1% by weight) were eliminated under vacuum overnight. For the formation of *in situ* sim IPNs, the mold was exposed to UV light (25°C), immediately after filling. Continuation of the process was identical to the synthesis of *in situ* seq IPNs. Three compositions were mainly prepared: 35/65, 50/50, and 60/40 PU/PS by weight. Transparent *in situ* seq PU/PS or hazy *in situ* sim PU/PS IPNs films, 0.7 mm thickness, were thus obtained.

Apparatus and characterization

The polymerization reactions were followed *in situ* by Fourier transform infra-red spectroscopy (Bomem Michelson MB 155 equipped with a Specac heating chamber). Generated by an external source (UVP Spot-cure), UV light was introduced through a flexible light guide positioned at an angle of 60° to the cell in order not to interfere with the incident IR beam. A sample of the initial reactive mixture was injected in a cell formed by two NaCl windows and a Teflon spacer. Scanning resolution was 2 cm⁻¹ and 10 consecutive scans were averaged for each spectrum. The progress of PU formation was monitored by following the decrease with time of the normalized absorbance of the characteristic NCO peak at 2270 cm⁻¹, and the progress of the radical copolymerization was evaluated from the decrease of the absorption band at 1630 cm⁻¹, assigned to the stretching mode of vinyl groups. The peak located at 1690 cm⁻¹ corresponding to the

TABLE I
Glass Transition Temperature (T_g) and Calculated Phase Composition According to the Fox Equation

IPN ^a PU/PS	Lower T_g (°C)	Upper T_g (°C)	Phase composition			
			PU-rich phase		PS-rich phase	
			PU (wt %)	PS (wt %)	PU (wt %)	PS (wt %)
100/0	-30		100	0	0	0
75/25	-17	35 ^b	83	17	39	61
60/40	-13	67	83	17	27	73
50/50	-13	79	83	17	22	78
35/65	-13	99	83	17	11	89
25/75	-13	125	83	17	0	100
0/100		125	0	0	0	100

^a PU based on Arcol® 1010 (MW = 1000 g/mol).

^b determined by curve deconvolution.

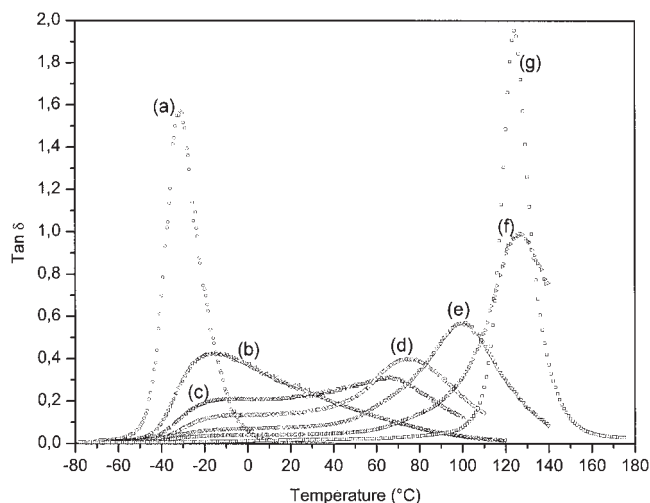


Figure 2 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* seq PU/PS IPNs of various compositions: (a) 100/0; (b) 75/25; (c) 60/40; (d) 50/50; (e) 35/65; (f) 25/75; and (g) 0/100. PU is based on Arcol 1010 (1000 g/mol).

isocyanate carbonyl was taken as an internal standard. Reaction conversion was calculated by the Beer-Lambert law from the change of normalized absorbance.

Dynamic mechanical analysis (Metravib RAC 815 viscoanalyser) were performed to determine the glass transition temperature (T_g) of the IPN films. T_g was taken as the maximum of the loss tangent ($\tan \delta$). Experiments in the tensile mode were done from -70 to 150°C at a fixed frequency of 5 Hz and a heating rate of $2^\circ\text{C}/\text{min}$, under dry nitrogen on rectangular specimens with a dimension of $30 \times 5 \times 0.7 \text{ mm}^3$.

Small-angle X-ray scattering (SAXS) data were obtained using a Nano Star diffractometer equipped with a two-dimensional position sensitive detector (Hi Star, Bruker) located at 102.6 cm from the sample position. Copper $K\alpha$ radiation was used. Measurements were carried out under vacuum to minimize air scattering. The measured intensities were normalized to the sample absorption and thickness, to the primary beam fluctuations, to the nonlinearity of the detector, by using an internal standard.

RESULTS AND DISCUSSION

In situ sequential IPNs

It is well known that the glass transition behavior of multicomponent materials is mostly affected by the miscibility of the components. Shape and position of the loss factor curves are commonly used to obtain information about the phase state.⁵ Figure 1 shows the loss factor ($\tan \delta$) as a function of temperature for two *in situ* seq IPNs, differing by the temperature conditions of synthesis. Both materials exhibit two distinct

glass transitions, typical of phase separation. It can also be seen that the inward shift of the transitions as compared with those of the individual components is larger for the photopolymerized (at 25°C) material than for the thermal (prepared at 60°C , using AIBN) *in situ* seq IPN, because of higher viscosity and reduced diffusion rate at room temperature. In addition to the viscoelastic properties, the transparency of the films is a qualitative criterion to estimate the miscibility thanks to the noticeable difference in refractive index, n , of the components ($n_{\text{PU}} = 1.47$, $n_{\text{PS}} = 1.59$). The photopolymerized *in situ* seq IPNs films are transparent (90% of light transmission at 589 nm) whereas the thermal *in situ* seq IPNs look blue-white opalescent,⁶ indicating larger domains for the latter IPNs.

A series of *in situ* seq IPNs with various compositions was prepared, and their glass transition temperatures are reported in Table I. Their $\tan \delta$ vs. temperature curves appear on Figure 2, together with the plot of the individual networks. Information about phase miscibility was deduced from the number, location, and shape of the transitions. It can be seen in Figure 2 that the upper transition is shifted toward lower temperatures, with subsequent broadening, when decreasing the PS content. However, the low temperature transition seems not to move with composition, only the shape of the peak changes. The composition of the phases was estimated by application of the Fox equation⁷ to these IPNs:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_{g1} and T_{g2} represent the glass transition temperature of the individual polymer 1 and 2, respec-

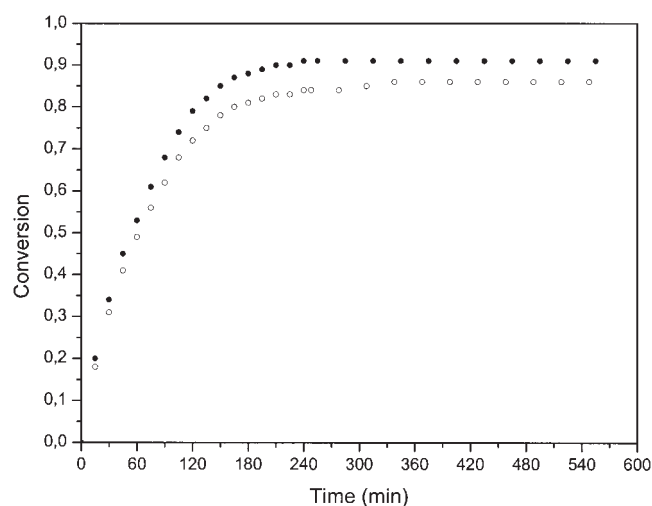


Figure 3 Conversion of vinyl groups vs. time for *in situ* seq IPNs of various composition: (○) 35/65; (●) 50/50. PU is based on Arcol 1010 (1000 g/mol).

TABLE II
Irradiation Time Required for Reaching Styrene End-Conversion under Different Experimental Conditions

<i>In situ</i> seq IPN PU/PS	<i>In situ</i> sim IPN PU/PS	PU elastic chain length (g/mol)	DVB content (wt %)	Time (h)
25/75		1000	5	8
35/65		4000	5	10
35/65		2000	5	8
35/65		1000	5	6
	35/65	1000	5	12
35/65		1000	0	9
50/50		4000	5	9
50/50		2000	5	7
50/50		1000	5	5.5
	50/50	1000	5	11
60/40		1000	5	5
75/25		1000	5	4

tively, and w denotes the weight fraction. The calculated compositions are reported in Table I. At every composition, the amount of PS present in the PU-rich phase is the same and therefore the glass transition temperature of that phase does not change. Consequently, the extent of phase separation is not governed by the rate of PS network formation, which varies with composition as seen in Figure 3. In the course of the *in situ* seq process, polymerization of styrene takes place in a topologically confined environment, i.e., within the preformed PU network, and phase separation develops according to a spinodal mechanism: phase separation occurs early in the process, at rather low conversion,⁸ when the growing chains have reached a critical length. The extent of phase separation is further stopped by gelation, i.e., formation of a tridimensional crosslinked structure and new topological en-

tanglements. Thus, for every composition, gelation of styrene takes place after the same given time of reaction. From the kinetical curves (Fig. 3) and data listed in Table II, it can be concluded that the extent of phase separation depends on the PU/PS ratio. As the PS content increases, the rate of the chain (co)polymerization increases, and the time to reach the end-conversion is thus reduced.

The fact that no displacement in T_g of the PU-rich phase is observed when varying the overall composition could be explained by considering that phase separation occurs because of the growth of molecular weight in the course of reaction, and arises from the inherent thermodynamic incompatibility of the components only. The results indicate that the *in situ* seq process is thermodynamically controlled. This might be possible since the segregation rate, at room temperature, is faster than the rate of formation of PS.

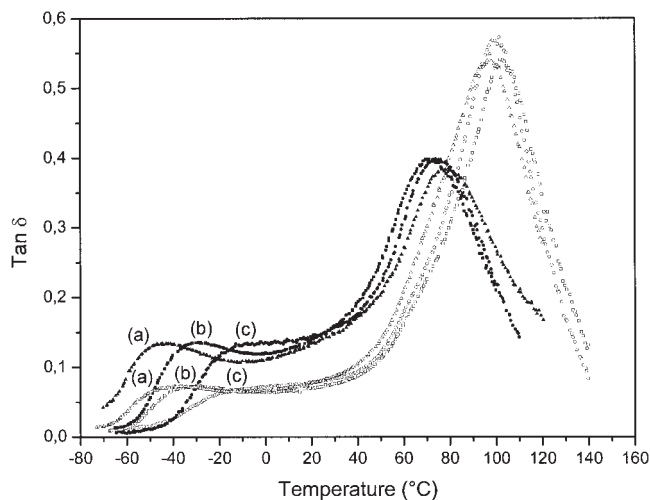


Figure 4 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* seq PU/PS IPNs of various composition: (open symbols) 35/65; (full symbols) 50/50. PU is based on (a) Arcol 1025 (4000 g/mol); (b) Arcol 1020 (2000 g/mol); and (c) Arcol 1010 (1000 g/mol).

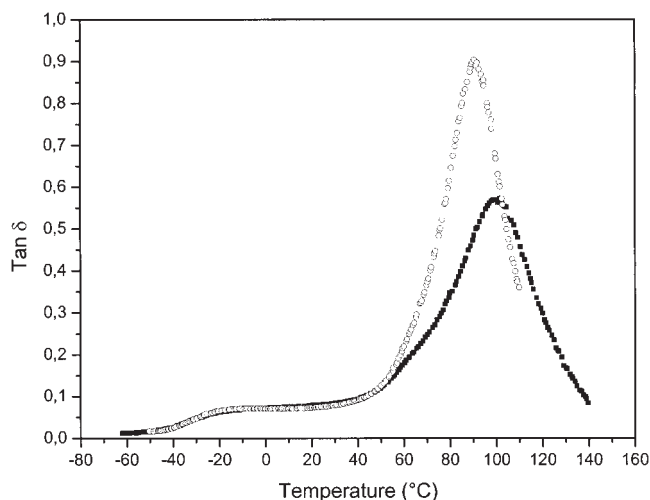


Figure 5 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* seq PU/PS IPNs of various crosslink density: (■) PS means 95/5 poly(S-co-DVB); (○) linear homopolystyrene. PU is based on Arcol 1010 (1000 g/mol).

TABLE III
Glass Transition Temperatures (T_g) of Various
In Situ seq PU/PS IPNs

PU/PS	PU elastic chain length (g/mol)	Lower T_g (°C)	Upper T_g (°C) ^a
100/0	1000	-30	—
50/50	1000	-13	75
35/65	1000	-13	99
100/0	2000	-44	—
50/50	2000	-29	70
35/65	2000	-29	102
100/0	4000	-50	—
50/50	4000	-40	78
35/65	4000	-40	98

^a T_g of individual PS network (0/100) is equal to 125°C.

The influence of the introduction of crosslinks, i.e., steric hindrances, on the extent of miscibility is shown in Figures 4 and 5, for PU and PS, respectively. Figure 4 compares loss tangent vs. temperature plots of *in situ* seq IPNs with various compositions and PU crosslink densities. Note that the latter was increased by simply using macrodiols of lower molecular weights, i.e., 4000 to 1000 g/mol, as elastic chains of the PU networks (which are formed by end-linking). As a consequence, the T_g of these PUs are located at different temperatures. However, there is a shift toward higher

temperature of the T_g of the PU-rich phase in IPN form, compared with the T_g of the corresponding individual PU. That inward shift is maximum when the PU is the most densely crosslinked (Table III). Also, the lower T_g , which corresponds to the PU-rich phase remains unchanged with composition for full IPNs and semi-IPNs as well. On the other hand, concerning the upper transition (Fig. 5), T_g increases as expected, when the PS chains are crosslinked, and the peak intensity decreases because of reduction of the degree of freedom. But, when compared with the T_g of the corresponding individual linear or crosslinked PS, the T_g of the *in situ* seq IPNs or semi-IPNs seems to be unchanged. This result indicates that an incomplete state of phase separation is obtained, however the crosslink degree of the polymer which forms second may be. These findings were confirmed by SAXS measurements, see Figure 6. Except in the small q region, the scattering curves are independent of the crosslink density of PS.

Assuming that the same weight fraction of PU causes thermodynamic incompatibility with PS, and from the kinetics of polymerization, Figure 7 and Table II, miscibility in *in situ* seq IPNs is not further dependent on the crosslink density of the preformed PU network, only the size of the domains is modified with an apparent reduction of the extent of phase

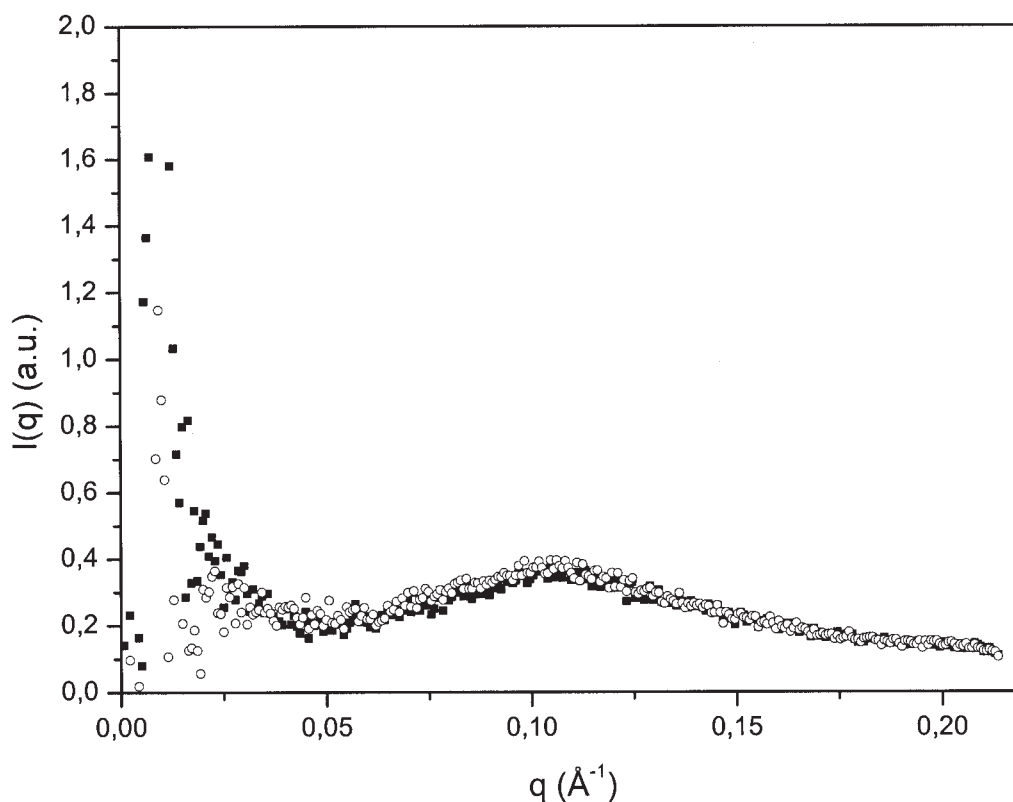


Figure 6 SAXS profiles, scattering intensity $I(q)$ vs. scattering vector q for *in situ* seq 35/65 PU/PS IPNs of various crosslink density: (■) PS means 95/5 poly(S-co-DVB); (○) linear homopolystyrene. PU is based on Arcol 1025 (4000 g/mol).

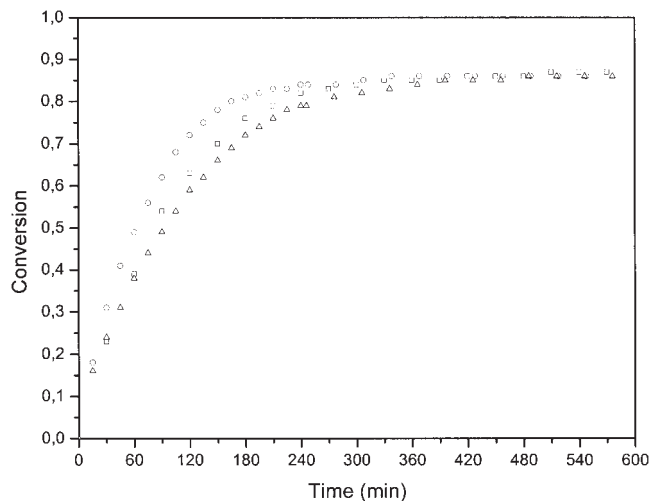


Figure 7 Conversion of vinyl groups vs. time for *in situ* sequential PU/PS IPNs of various crosslink density of PU: PU is based on (Δ) Arcol 1025 (4000 g/mol); (\square) Arcol 1020 (2000 g/mol); (\circ) Arcol 1010 (1000 g/mol).

separation. Rharbi et al.⁹ have characterized the interface of crosslinked poly(methyl methacrylate) and PU sequential IPNs from energy transfer studies. They came to the conclusion that the extent of interfacial mixing is controlled by incompatibility of the polymer pair, and not by the level of polymer crosslinking. Hence, for two different but similar systems, using different ways of characterization, the *in situ* sequential IPN synthesis proceeds under the control of thermodynamic incompatibility of the components.

In situ simultaneous IPNs

In Figure 8 are shown $\tan \delta$ vs. temperature curves of *in situ* simultaneous PU/PS IPNs with various compositions, in comparison with the curves of the individual PU and PS networks. Obviously, the curves indicate phase-separated materials but morphologically quite different from *in situ* sequential IPNs, see Figure 2. The interval between T_g of the pure networks and the corresponding T_g of the "simultaneous" samples is lower than that of the "sequential" samples. For *in situ* simultaneous IPNs, both the low transition peak and the high transition peak are well individualized, and consequently, the loss value of the plateau region between the two transitions is lower than that for *in situ* sequential IPNs. All these observations indicate a higher extent of phase separation for *in situ* simultaneous IPNs.

The upper peak, which is broad, can be decomposed into two narrow peaks (Figs. 9 and 10): one centered at T_g of the pure PS and another one located at T_g of the PS-rich phase mentioned for *in situ* sequential IPNs. Therefore, various levels of phase separation would coexist in these *in situ* simultaneous IPNs. The resulting morphology of these *in situ* simultaneous PU/PS IPNs depends on the time

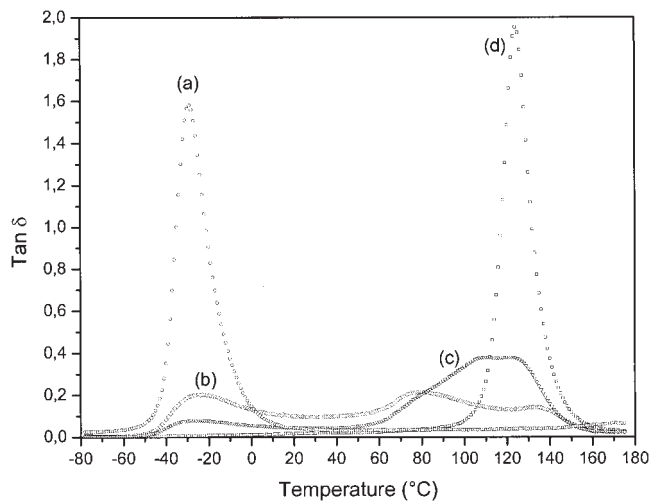


Figure 8 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* simultaneous PU/PS IPNs of various composition: (a) 100/0; (b) 50/50; (c) 35/65; and (d) 0/100. PU is based on Arcol 1010 (1000 g/mol).

sequence of the following events: (i) formation of the PU network, (ii) formation of PS, and (iii) phase separation. Considering the kinetic curves, which show (Fig. 11) that PU network formation takes place after an appreciable conversion degree of styrene (co)polymerization, phase separation occurs first, developing large domains due to a rather low viscous reactive medium. The variation of the entropy of mixing becomes negative, and the free energy of mixing becomes positive. Both reactions evolve in two phases of variable composition. Gelation of one of the components impedes further gross phase separation and the system is frozen at a nonequilibrium structure of incomplete phase separation. Consequently, two levels

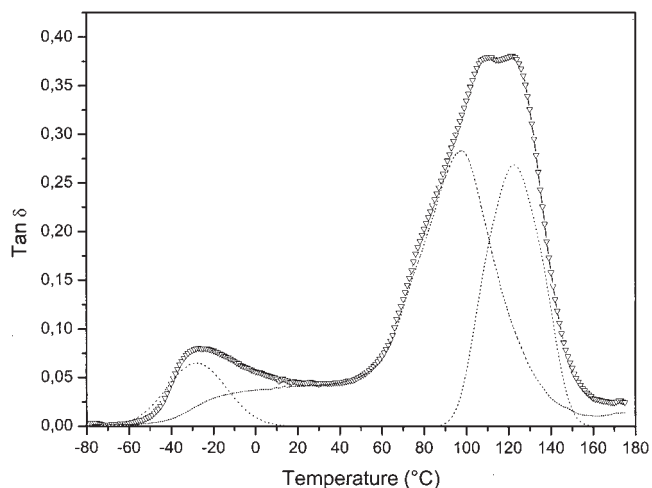


Figure 9 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* simultaneous 35/65 PU/PS IPNs and deconvolution curves (dotted line).

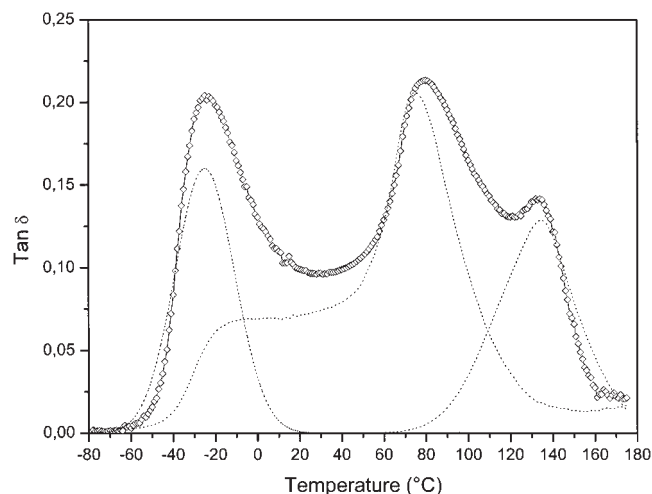


Figure 10 Loss factor ($\tan \delta$) vs. temperature curves for *in situ* sim 50/50 PU/PS IPNs and deconvolution curves (dotted line).

of phase separation coexist for *in situ* sim IPNs: a macroscopic phase separation, which develops from the onset of both reactions to the gelation of one component, and a microphase separation, which is thought to be associated with the decreased chain mobility after gelation. The microheterogeneous morphology obtained for these *in situ* sim IPNs, and consequently their properties, depend on composition and on the kinetics of reaction together with the thermodynamic incompatibility of the components. Hence, the extent of macroscopic phase separation in *in situ* sim IPNs can be reduced by accelerating gelation of the system. Therefore, Arcol 1025 was replaced by another poly(oxypropylene glycol), also having a

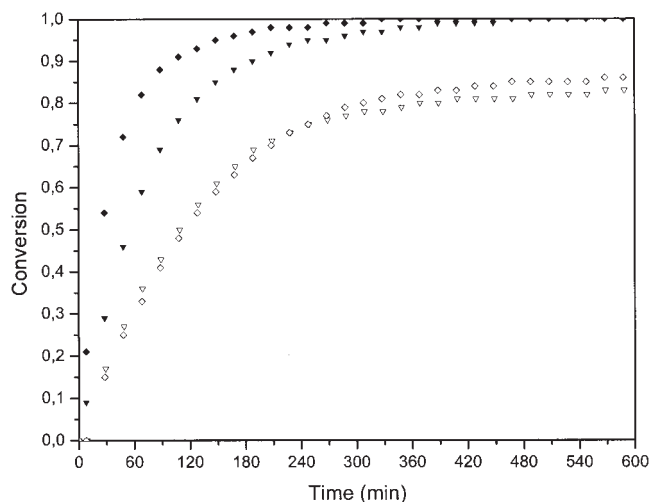


Figure 11 Conversion of vinyl groups (full symbols) and isocyanate groups (open symbols) vs. time for *in situ* seq IPNs of various composition: (∇, ∇) 35/65; (\blacklozenge, \diamond) 50/50. PU is based on Arcol 1010 (1000 g/mol).

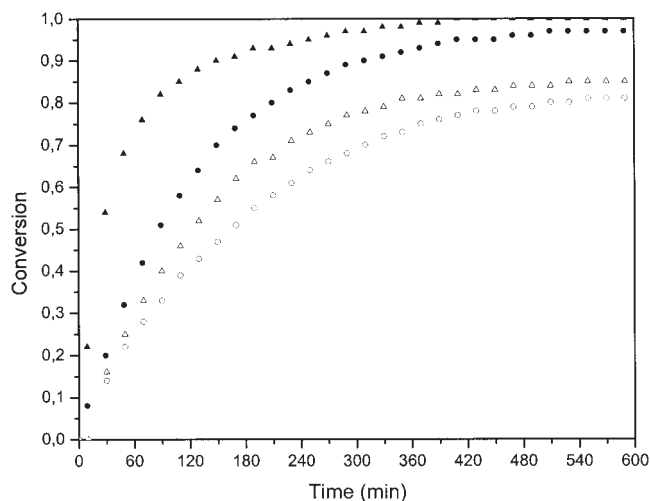


Figure 12 Conversion of vinyl groups (full symbols) and isocyanate groups (open symbols) vs. time for *in situ* seq 50/50 IPNs using macrodiols (MW = 4000 g/mol) of various reactivity: ($\blacktriangle, \triangle$) secondary OH; (\bullet, \circ) primary OH.

molecular weight of 4000 g/mol, but bearing primary OH groups, which are known to be more reactive toward isocyanate groups than the standard secondary hydroxy groups. As expected, the rate of PU network formation was increased as can be seen in Figure 12, and because of an earlier gelation of the medium, macrophase separation is further impeded as it is the case for *in situ* seq IPNs. The morphology of these "accelerated" *in situ* sim IPNs should be very similar to that of *in situ* seq IPNs, as suggested by the similarity of their $\tan \delta$ vs. temperature curves (Fig. 13). Additionally, as a confirmation of it, the *in situ* sim IPN thus prepared exhibits high optical clarity like the corresponding *in situ* seq IPN.

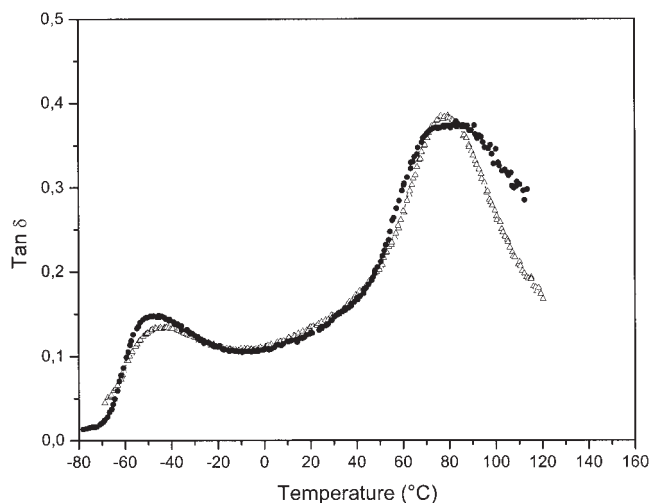


Figure 13 Loss factor ($\tan \delta$) vs. temperature curves for (\bullet) *in situ* sim 50/50 PU/PS IPNs and for (\triangle) *in situ* seq 50/50 PU/PS IPNs. PU is based on Arcol 1025 (4000 g/mol).

CONCLUSIONS

The extent of phase separation in IPNs made from PU and PS, which are an incompatible pair, depends on the experimental conditions. Two levels of phase separation can be distinguished in IPNs made according to the *in situ* "simultaneous" process: (i) a macroscopic phase separation into almost pure phases, resulting from the competition between the rate of network formation and the rate of phase separation during the early stage of synthesis, i.e., before gelation of the reaction mixture, and (ii) a microphase separation thermodynamically controlled by the inherent level of miscibility of the constituents. It appeared that the concept of "forced miscibility" imparted to IPNs is not verified as the composition and the crosslink density of the components have no effect on the multiphase structure.

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