

Relationships between Polymerization Activating Systems and Viscoelastic Properties of the Subsequent Polyurethane/Poly(*tert*-butyl acrylate) Interpenetrating Polymer Networks

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Received 23 April 1996; accepted 26 July 1996

ABSTRACT: To date, most interpenetrating polymer networks (IPNs) are developed for slow processes such as casting or coating. For industrial manufacturing, fast-reactive polymer processing is often required. Simply increasing the amount of catalyst and/or free-radical initiator shows some limitations. Also, increasing too much temperature may cause degradation or side reactions. For polyurethane/polyacrylate IPNs, more or less simultaneous formation of the two networks, with over 97% conversion was obtained after 4 to 6 min at 110°C, using appropriate catalyst/initiator combinations. Depending on the relative kinetics of network formation, either one, two, or multiple transitions were found for a given composition. Kinetics of formation and phase behavior have been investigated by Fourier transform infrared spectroscopy and dynamic mechanical analysis. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 951–958, 1997

Key words: interpenetrating polymer networks; IPNs; polyurethane; polyacrylic network; kinetics; phase behavior

INTRODUCTION

An interpenetrating polymer network (IPN) is defined as a combination of two crosslinked polymers held together by physical interlocking.^{1,2} There are many subclasses of IPNs, depending on their preparation schemes. In the one-step process, also called *in situ* process,³ all components necessary to build up the final IPN are first mixed together, and the two networks are formed more or less simultaneously by noninterfering reaction mechanisms. In most cases, phase separation occurs during the synthesis and the resulting two-phase morphology, which is difficult to predict, affects the overall properties. The morphology of

the IPNs is at a quasi-equilibrium state determined by a balance between the chemical process of network formation and the physical process of phase separation. Informations regarding both the reaction kinetics and development of morphology during synthesis are essential to optimize a given IPN system.

Although detailed analyses of the polymerization kinetics have been reported in the literature,^{4–10} most articles are related to relatively slow processes occurring under mild temperature conditions. For industrial manufacturing, a fast-cure process is often required, and some polyurethane-based IPNs have been developed successfully in recent years.^{11–16} However, there is still a lack of information concerning the reaction kinetics. One reason might be the difficulty in very fast reactions to interrupt the process at different stages and analyze the unreacted monomer mixture. The use of a Fourier transform infrared

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Table I Raw Materials

Designation	Description	Supplier
N100	Mixture of biuret homologues derived from hexamethylene diisocyanate (Desmodur® N100); density = 1.14; 5.02 NCO/kg	Bayer AG
POPG	Poly(oxypropylene glycol) (Arcol® 1004); $M_n = 450$ g/mol; hydroxyl content = 4.4 mol/kg	ARCO Chemicals
tBA	<i>tert</i> -Butyl acrylate (98%); stabilized with 75 ppm of 4-methoxyphenol	Aldrich
TRIM	1,1,1-Trimethylolpropane trimethacrylate; inhibitor: 100 ppm methylethyl hydroquinone	Degussa
K19	Di- <i>n</i> -butyl tin dilaurate (Kosmos® 19); tin content = 18.5 wt %	Goldschmidt AG
K29	Stannous octoate (Kosmos® 29); tin content = 28.6 wt %	Goldschmidt AG
AIBN	2,2'-asobisisobutyronitrile (98%)	Merck
BPO	Benzoyl peroxide (97%)	Fluka
TBPIN	<i>tert</i> -Butyl peroxy isononanoate	SCPO France

(FTIR) spectrophotometer, which gives numerous spectra in little time, would overcome that experimental difficulty.

The purpose of the present investigation is first to define activating systems that allow the IPN to be formed in less than 5 min at a processing temperature of 110°C. Kinetic results from FTIR spectroscopy are presented for a 50/50 polyurethane/poly(*tert*-butyl acrylate) IPNs. Cross-linked polyurethane (PUR) is obtained by a step-polyaddition of an aliphatic pluriisocyanate with a poly(oxypropylene glycol) (POPG). The polyacrylic network is formed by free-radical copolymerization of *tert*-butyl acrylate (tBA) with trimethylolpropane trimethacrylate (TRIM). Various combinations of two tin catalysts with three free-radical initiators were examined. Then, effects of the relative chemical reaction rate on dynamic mechanical properties are reported.

EXPERIMENTAL

Materials

The raw materials used are listed and described in Table I. The poly(oxypropylene glycol) (POPG) was dried at 60°C under vacuum for 12 h, just before use. The aliphatic pluriisocyanate (N100) was used as received and its functionality determined by standard titration with di-*n*-butylamine.¹⁷ The monomers, *tert*-butyl acrylate (tBA) and trimethylolpropane trimethacrylate (TRIM), were stored over 4 Å molecular sieves for at least 2 weeks before use, but not otherwise purified.

The tin catalysts (K19 and K29) and the free-radical initiators (AIBN, BPO, and TBPIN) were used as received.

Synthesis

PUR/PtBA IPNs were prepared by dissolving at room temperature and under circulation of nitrogen, the required amounts of N100 and POPG ($[\text{NCO}]/[\text{OH}] = 1.07$) in a mixture of tBA monomer containing 5 wt % of TRIM, and 1 wt % of initiator(s). The catalyst (1 wt %) was added last. The PUR/tBA ratio in all cases was the same (50/50 by mass). The mixture was poured into a metallic mold to form films of about 2 mm thickness. The mold was then placed in a preheated oven at 110°C and kept at this temperature for 30 min. The IPN films thus formed were removed from the mold after cooling, and used for dynamic mechanical characterization without further thermal treatment. For kinetic analysis, the previous mixture was injected in a cell formed by two NaCl windows separated by a 25 μm thick gasket. The individual constituent networks were prepared similarly: the crosslinked PUR was formed in a 50 wt % ethyl acetate solution and the polyacrylic network was obtained in bulk.

Kinetics

Fourier transform infrared (FTIR) spectroscopy was used to study the kinetics of IPN formation. Spectra were collected using a Nicolet 60SX spectrophotometer equipped with a Specac heating

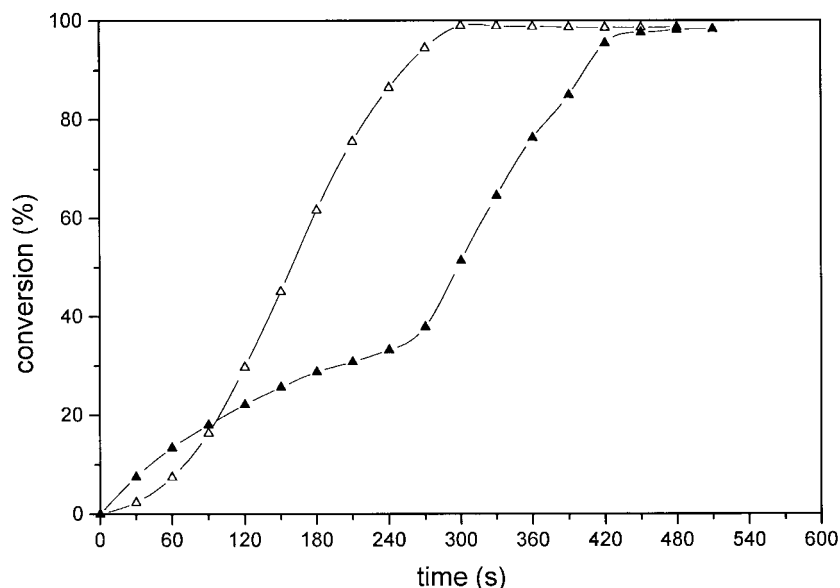


Figure 1 Conversion profiles of PUR (Δ) and PtBA (\blacktriangle) at 110°C . Activating system: K19 and AIBN.

chamber. Heating of the chamber was monitored so that the sample was allowed to reach the desired temperature (110°C) after approximately 1 min. Reaction conversion was calculated from the change of the normalized absorbance of the NCO peak at 2275 cm^{-1} and the C=C peak at 1640 cm^{-1} . The CH_2 stretching vibration at 2870 cm^{-1} was used as an internal standard.

Dynamic Mechanical Measurements

A Rheometrics Solids Analyzer (RSA II) was used to determine the dynamic modulus-temperature behavior from -50 to 150°C with a heating rate of 2°C per min. The measurements were conducted under dry nitrogen in a compressive mode at a constant angular frequency (10 rad/s) and fixed amplitude (0.1%). The test specimen were discs of films, diameter 15 mm , thickness 1.7 mm . Glass transition temperatures were identified by the temperature corresponding to the maximum value of the loss factor, $\tan \delta$.

RESULTS AND DISCUSSION

Figure 1 shows the kinetics of formation of an *in situ* PUR/PtBA IPN using 1% dibutyltin dilaurate (K19) as catalyst and 1% azobisisobutyronitrile (AIBN) as free-radical initiator. Conversion

of PUR reaches 99% after almost 5 min of reaction. However, in these conditions, polymerization rate of tBA is relatively slow despite autoacceleration (Trommsdorff effect), and formation is complete only after 7 min. A possible reason is an early consumption of radicals (decomposition temperature of AIBN is 56°C). To increase the rate of formation of PtBA, the idea was to supply the medium continuously with fresh radicals, using initiators that have different half-life times, i.e. which decompose at different temperatures. Therefore, a combination of AIBN (0.5%) and benzoyl peroxide (BPO) (0.5%) was used, and the result on the conversion versus time curves is shown in Figure 2. As expected, the rate of PtBA formation is increased but incomplete conversion of polyurethane occurs (maximum 87%). This phenomenon was previously observed during the formation of *in situ* simultaneous PUR/PMMA IPNs at 60°C , and was attributed to vitrification of the medium.¹⁸ However, this explanation does not apply here as reaction is conducted largely over the glass transition temperature of the network components. One may assume eventual interaction of the tin catalyst with BPO, or with the traces of water in BPO.

The next tentative was to double the amount of catalyst. The result is that the PUR conversion vs. time curve reaches a plateau at 90% conversion after 4 min of reaction, similarly to what was

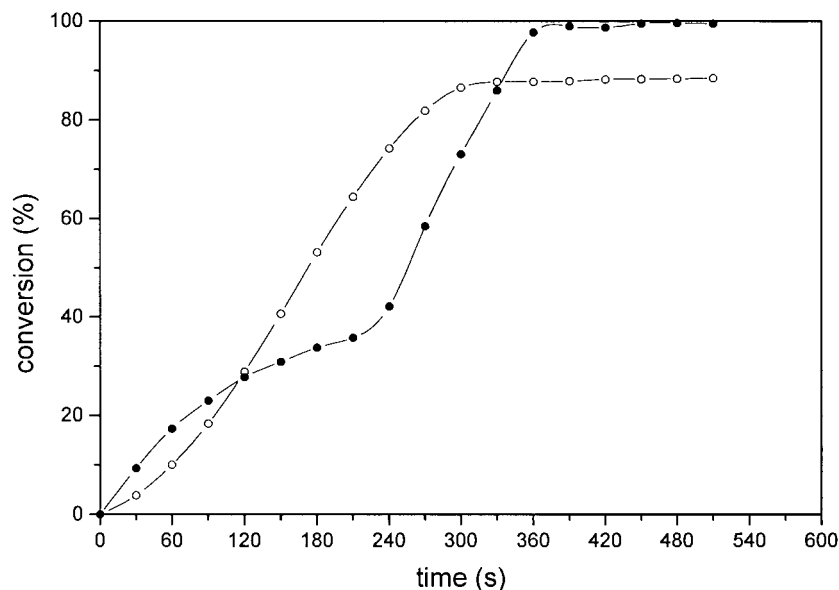


Figure 2 Conversion profiles of PUR (○) and PtBA (●) at 110°C. Activating system: K19 and AIBN + BPO.

observed with less amount of catalyst. Another tentative was to switch from dibutyltin dilaurate (Sn^{IV}) to stannous octoate (Sn^{II}) (K29), which is a more efficient isocyanate-alcohol catalyst.¹⁹ However, in presence of radicals, the catalytic activity of K29 is less than expected due to oxidation of tin from valence II to valence IV.²⁰ Concurrently, when combined with AIBN,²¹ the 1 : 1 cyclic complex thus formed decomposes more easily into radicals than AIBN at a given temperature, therefore accelerating the radical polymerization. The synergical effect between K29 and AIBN is shown in Figure 3. As can be seen, the kinetics of network formation are rather identical for both components, and a simultaneous IPN is almost completely formed in less than 5 min.

Similarly to what was obtained by using the AIBN + BPO system, addition of *tert*-butyl peroxy isononanoate (TBPIN), an initiator that decomposes around 95°C,²² to AIBN speeds up the polymerization rate of tBA to such an extent that formation of the polyacrylic network occurred before that of polyurethane (Fig. 4). As previously seen, the presence of peroxy radicals impedes complete formation of the PUR network.

In conclusion of the kinetic studies related to the choice of an activating system, one has roughly obtained three types of *in situ* PUR/PtBA IPNs, which differ in order of network formation: one where the PUR network is formed first, an-

other where both networks form simultaneously, and finally one where the PUR is formed last. Logically, the morphology of these IPNs should be different.

The phase behavior of these IPNs have been investigated by means of dynamic mechanical analysis. From the peak of loss tangent, the glass transition temperature (T_g) of the individual constituent networks, PUR and PtBA, were found at -14 and 53°C , respectively. Considering the *in situ* sequential IPN obtained according to the kinetics displayed in Figure 2 using K19 as catalyst and AIBN + BPO as initiators, its viscoelastic behavior is shown in Figure 5: multiple transitions are seen, especially one major transition located at 14°C and a shoulder located at 39°C , which correspond to a polyurethane-rich phase and a polyacrylic-rich phase, respectively. Another peak appears at low temperature at -43°C and is assigned to a POPG phase due to incomplete PUR formation.

The "reverse" *in situ* sequential IPN for which PtBA network forms first shows two distinct transitions (Fig. 6). The lower transition corresponding to the PUR phase is shifted toward a higher temperature (8°C), and this shift suggests some phase mixing. However, the upper transition (found at 63°C) is unexpectedly higher than the T_g of the neat PtBA network, indicating almost pure PtBA phase. Perhaps, the presence of the

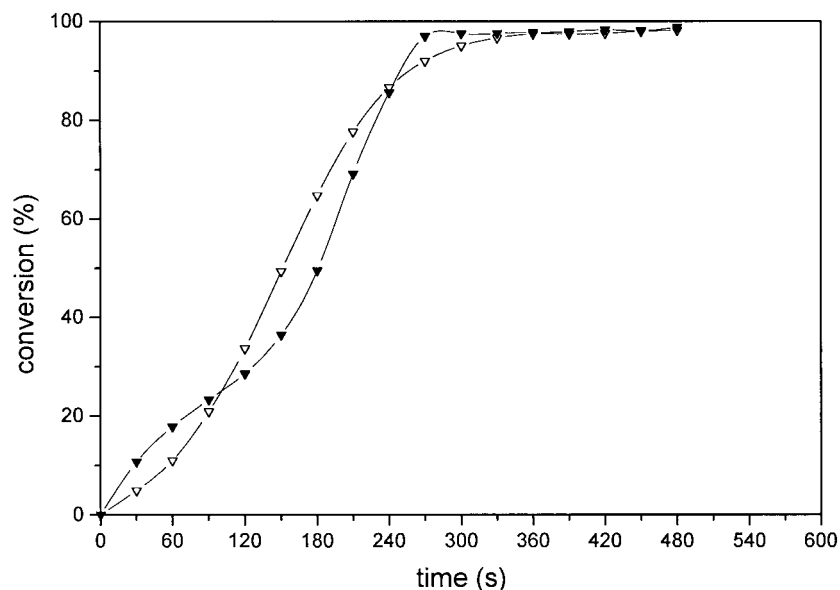


Figure 3 Conversion profiles of PUR (∇) and PtBA (\blacktriangledown) at 110°C. Activating system: K29 and AIBN.

PUR precursors, which act as diluent during the formation of the PtBA network leads to a higher crosslink density than for synthesis conducted in bulk.

Figure 7 represents the dynamic mechanical behavior of the *in situ* simultaneous PUR/PtBA

IPN obtained by using K29 and AIBN as catalyst and initiator, respectively. Apparently, only one transition is found at 22°C (maximum of $\tan \delta$), close to the theoretical T_g value (19.7°C) calculated from the Fox equation,²³ assuming a fully miscible system. This is an indication of a one-

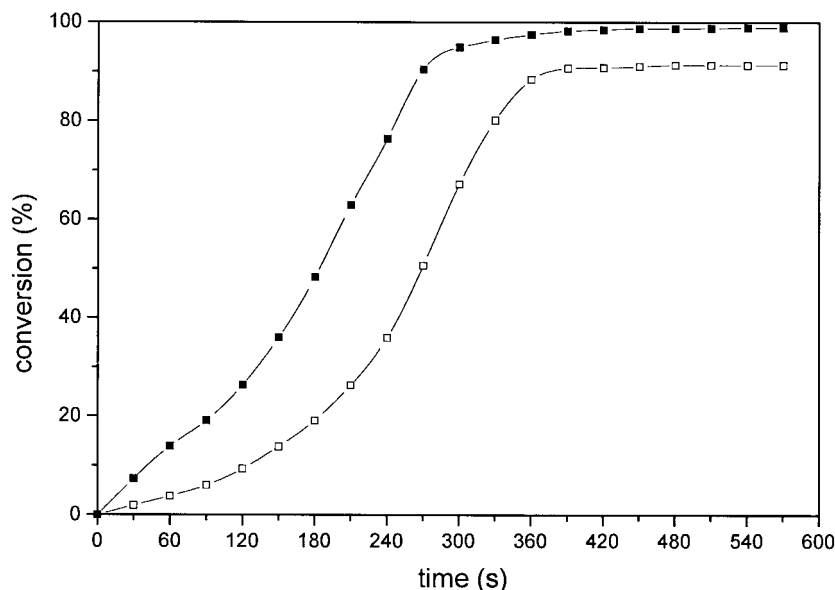


Figure 4 Conversion profiles of PUR (\square) and PtBA (\blacksquare) at 110°C. Activating system: K29 and AIBN + TBPIN.

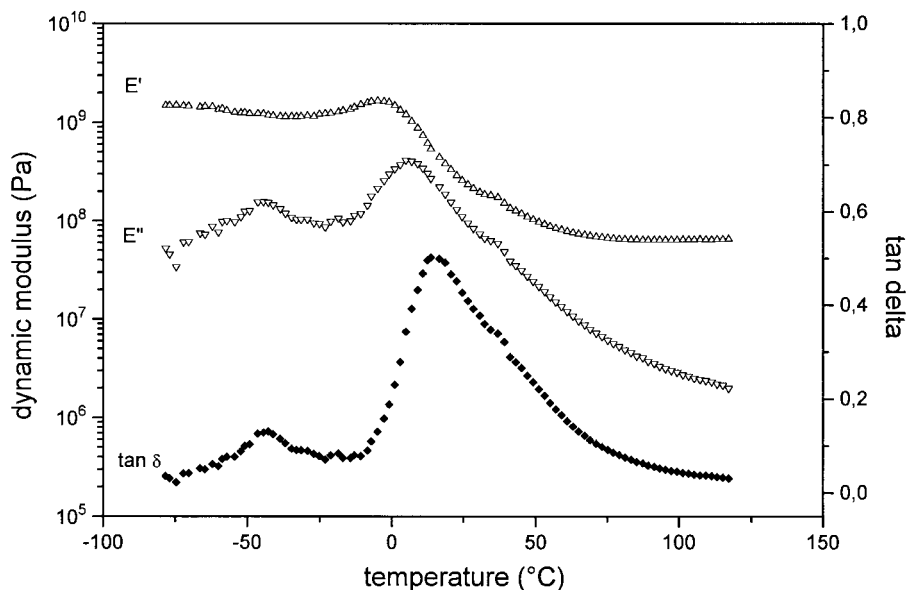


Figure 5 Dynamic mechanical spectra of the *in situ* sequential PUR/PtBA IPN.

phase morphology. Compared with the curves displayed in Figure 5, the loss tangent peak is reduced in temperature range and increased in intensity, thus confirming that the *in situ* simultaneous IPN is less phase-separated than the corresponding *in situ* sequential IPN.

Note that this applies to rapid network formation only, and that opposite results were found for

conventional *in situ* IPNs for which synthesis lasts several hours.²⁴ In a fast-cure process, topological interlocking of the crosslinked chains occurs before phase separation can take place, because of the slow kinetics of the latter. In a conventional (slow) process, when the chemical reactions start simultaneously (*in situ* simultaneous IPNs), phase separation begins at very low

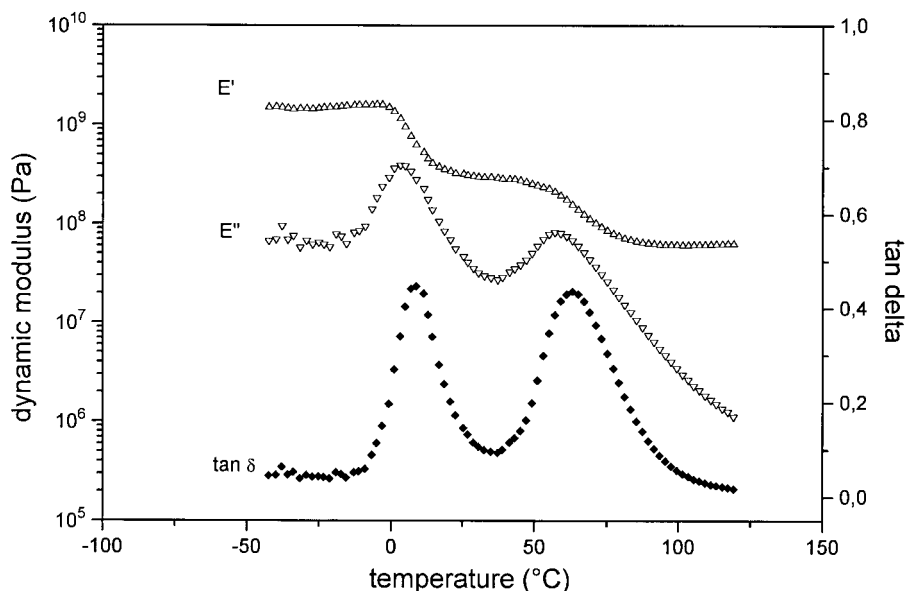


Figure 6 Dynamic mechanical spectra of the "reverse" *in situ* sequential PUR/PtBA IPN.

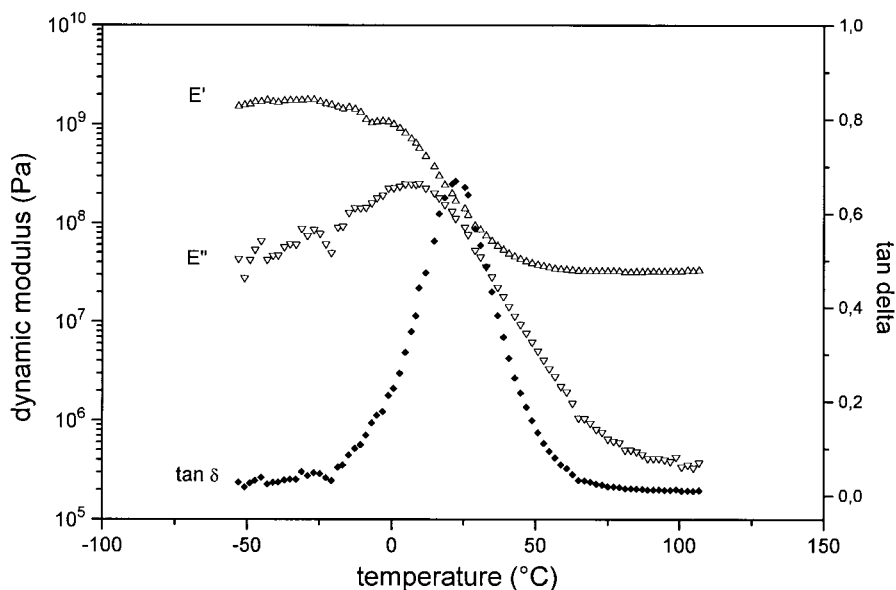


Figure 7 Dynamic mechanical spectra of the *in situ* simultaneous PUR/PtBA IPN.

conversions and is enhanced with increasing molecular weights. It is only when gelation of one component occurs prior to initiation of the other polymerization (*in situ* sequential IPNs) that phase separation is limited, because the formation of the second network is confined in the cage made by the first network.

CONCLUSION

The final morphology of *in situ* IPNs depends upon the degree of phase separation, which is, in turn, related both to the thermodynamics of the constituents and to the kinetics of network formation.

For a given system, it is generally admitted that increasing the chemical reaction rate prevents the diffusion of the reactants and subsequent phase separation. However, this statement has to be examined in terms of relative formation rates of each network. Bringing them closest to simultaneity results in reduction of the extent of phase separation. The above kinetic studies indicate that one-phase materials are obtained only with well-matched rates of the crosslinking reactions. Otherwise, in the case of nonsimultaneous gelation, the thermodynamic immiscibility is sufficient to generate more or less phase-separated IPNs. So far, despite detailed kinetic investiga-

tions, working out a given morphology and properties by a fast-cure process seems especially ticklish and hardly reproducible.

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