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Interpenetrating Chemical (Polyepoxide) and Physical (Poly(vinyl chloride)) Gels

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ABSTRACT: Low-concentration solutions of poly(vinyl chloride) (PVC) in (diglycydyl ether of bisphenol A/4,4′-diamino-3,3′-dimethyldicyclohexyl methane) monomers were observed to have the ability to form chemically reactive physical gels. The changes in rheological and optical properties were monitored as a function of time by the use of dynamic shear rheometry and light transmission, respectively. For a given PVC concentration, the isothermal behavior of these solutions is governed by the competition between physical gelation rate and reaction-induced phase separation rate. The temperature, ${}_{\mathrm{pg}}T_{\mathrm{ll}}$, at which physical gelation and liquid−liquid demixing occur simultaneously, was then defined. When curing temperature, T_{i}, is higher than ${}_{\mathrm{pg}}T_{\mathrm{ll}}$, the blend behaves like a classical amorphous thermoplastic-thermoset blend and the final heterogeneous structure consists of PVC-rich particles dispersed in a polyepoxide-rich matrix. When T_{i} is lower than ${}_{\mathrm{pg}}T_{\mathrm{ll}}$, the physical gelation rate is high enough to ensure the formation of a macroscopic PVC gel before any phase separation phenomenon. True interpenetrating chemical (polyepoxide) and physical (PVC) gels are then generated. The usual temperature-dependent function of the crystallization-induced physical gelation rate was found to be affected by the extent of the epoxy−diamine polycondensation reaction. The evolution of ${}_{\mathrm{pg}}T_{\mathrm{ll}}$ with PVC concentration is mainly governed by the concentration-dependent function of the physical gelation rate, resulting in an increase of ${}_{\mathrm{pg}}T_{\mathrm{ll}}$ with PVC concentration.

1. Introduction

When allowed to cross-link, polymers can undergo gelation, i.e., a transition from liquid to solid which causes dramatic changes to polymeric systems, especially to their macroscopic viscoelastic behavior. For structures that exhibit gellike behavior, two kinds of gels can be distinguished: (i) chemical gels in which cross-links are permanent covalent bonds and (ii) physical gels formed by aggregation of polymer chains in which cross-links are annealed and thermoreversible. Irrespective of the gel nature, the pregel state is experimentally characterized by a finite value of the static viscosity that diverges at the gel point, corresponding to the formation of an infinite macroscopic molecule in spatial extent coexisting with finite molecules. Gelation is theoretically described as a percolation transition[1,2] that implies universal critical behavior, on which system details are irrelevant. For instance, the following scaling law has been found to hold at the gel point whether chemical[3−13] or physical[14−18] cross-links are involved:

$$G'(\omega) \propto G''(\omega) \propto \omega^{\Delta} \tag{1}$$

where G' and G'' are the dynamic moduli as a function of angular frequency ω. It means that the sol−gel transition can be accurately determined using the frequency independence of the loss tangent, tan δ.

As all previously reported works on poly(vinyl chloride) (PVC) and other physical gels deal with nonreactive solvents, we will investigate in the present paper the behavior of PVC chains in reactive epoxy−diamine precursors of chemical gels. In a previous paper,[20] the selected epoxy−diamine system has been fully characterized in terms of kinetics of reaction, chemical rate constants, and time−temperature−transformation diagram. In this work, the chemical gel formation is achieved by isothermal heating in the presence of low PVC concentrations. The changes in rheological and optical properties are monitored as a function of time by the use of dynamic shear rheometry and light transmission, respectively. The measurements are carried out at different temperatures and PVC concentrations to investigate their effects on the blend behavior. The results are displayed on various diagrams and discussed in terms of reaction-induced liquid−liquid demixing and physical gelation kinetics.

2. Background

2.1. Polyepoxide Chemical Gels. Chemical gels are synthesized by a bulk reaction of a reactive fluid in which the average functionality of reactants is greater than 2. It is now well-established that for polyepoxides based on epoxy−diamine precursors the network buildup is statistical, leading to a perfectly homogeneous structure. The epoxy−diamine reaction mechanisms, involving the reaction of the primary amine hydrogen with an epoxy group followed by the secondary amine hydrogen reacting with another epoxy group, have been already described in detail.[19−24]

During isothermal cure, two structural transformations are expected to occur: chemical gelation and vitrification. As the extent of reactions/epoxy conversion at the chemical gelation point, x_{cg}, is fixed by the average functionalities of monomers[25] and the reactivity ratio of the primary and secondary amino groups,[26] the chemical gelation times, t_{cg}, obey an Arrhenius law as a function of temperature.[19,20] Vitrification involves a transformation from the liquid or rubbery state into the glassy state as a consequence of either the increase in molar mass before gelation or the increase in cross-link

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density after gelation. The vitrification time, t_{vitr} conceptually corresponds to the time at which the glass transition temperature of the reacting system, T_g reaches the cure temperature, T_i. After vitrification, the reactions are no longer controlled by the rate of chemical reaction but become diffusion-controlled. It has been shown that an excellent description of the diffusion process in the nonequilibrium state can be carried out for thermosets using glass transition theories.[21,27−29] These transformations are conveniently summarized in a time−temperature−transformation TTT diagram.[30] In such a representation, ${}_{\mathrm{cg}}T_g$ (usually called ${}_{\mathrm{gel}}T_g$) denotes the critical temperature at which chemical gelation and vitrification occur simultaneously. It also corresponds to the glass transition temperature of the chemical gel. At $T_i > {}_{\mathrm{cg}}T_g$, chemical gelation takes place isothermally before vitrification; at $T_i < {}_{\mathrm{cg}}T_g$, vitrification occurs first.

2.2. Poly(vinyl chloride) Physical Gels. At a concentration higher than c_{pg}, the critical physical gelation concentration, solutions of PVC in numerous solvents solidify on cooling and subsequent isothermal aging.[15−18,31−41] This phenomenon, known as thermoreversible gelation, results from the formation of a physical three-dimensional network of PVC chains in the solvent. The gel is fully reversible and can be restored to its original solution by heating. The concentration-dependent melting temperature, T_m of aged gels, which corresponds to the temperature transition from the gel state to the sol state, is usually determined by following changes in $G'(\omega)$ profiles with temperature, the sol state being characterized by the terminal behavior of $G'(\omega) \propto \omega^2$ at low frequencies.[18]

The presence of noncovalent cross-links complicates any physical description of the network properties because their number and position fluctuate with time and temperature.[42] Furthermore, the cross-links act not at a point on the chain as do covalent cross-links, but instead involve more extended junction zones. Similar to most physically gelling systems, the details in this junction structure for PVC gels is not completely understood. PVC gels have been described by a fringed-micelle structure model where the network is composed of small crystallite domains with flexible chains connecting the junctions.[31,37] Another model, describing the formation of the network structure by an array of fibrous crystals,[32−34,40,41] highlights the difficulty in experimentally characterizing the complex junction structure of these systems. Besides experimental examination of the junction structure, a theoretical model based on the junction multiplicity has been proposed to analyze the junction structure in thermoreversible gels.[43,44]

However, the microstructure and hence macroscopic properties of crystallization-induced PVC gels are dependent not only on thermodynamic parameters such as temperature and concentration but also on the thermal history of the sample.[45] This constitutes an additional difficulty in characterizing such out of equilibrium systems. More generally, the way these systems can be viewed through a macroscopically measurable parameter depends on the difference between the time scale of the measurement and the time scale of the physical aging process.

Usually considered as the inverse of the physical gelation time, the physical gelation rate, t_{pg}^{-1} can be expressed as the combination of a concentration-dependent function and a temperature-dependent function.[46−49] Studying the gelation rate vs concentration and temperature has been found to be a powerful tool for providing information about the macroscopic and microscopic mechanism of gelation, respectively.

2.3. Reaction-Induced Phase Separation in Thermoplastic−Thermoset Blends. Assuming the thermoplastic solutions in the thermoset precursors to be initially homogeneous, the increase in the molar mass of the epoxy−diamine copolymer during curing may result in liquid−liquid phase separation, even if the temperature is kept constant, due to the decrease in entropy of mixing. Such a well-known reaction-induced phase separation process[50−58] can be very simply detected by the fact that the solutions become cloudy. The final morphology in resulting thermoplastic−thermoset blend is strongly dependent on the complex competition between phase separation and polymerization rates. In particular, when considering the dynamics of phase separation, a chemical quench from the miscible one-phase region into the metastable or unstable region results in nucleation and growth or spinodal demixing, respectively. The complexity of these systems has led to a limited number of theoretical attempts to explain the phase separation behavior[53−55] despite many experimental studies.

However, the knowledge of the initial critical thermoplastic concentration prior to reaction, c_{crit}, where binodal and spinodal curves meet, has been shown to enable good qualitative predictions about the behavior of the blend during reaction. Indeed, in the case of a branched epoxy−diamine polymer prior to gelation which obeys classical statistics, the critical concentration does not vary much with the extent of reaction and it is therefore not necessary to know at what stage of curing the blend becomes immiscible to predict its behavior. Hence, for off-critical composition, phase separation is expected to produce either a dispersed thermoplastic-rich phase in a continuous thermoset-rich phase (c significantly lower than c_{crit}) or a dispersed thermoset-rich phase in a continuous thermoplastic-rich phase (c significantly higher than c_{crit}). On the other hand, for concentrations located in the vicinity of c_{crit}, the structure will be bicontinuous.

3. Experimental Section

3.1. Materials. The linear polymer used in this work is a commercial PVC made through bulk polymerization by Elf-Atochem (GB1040).

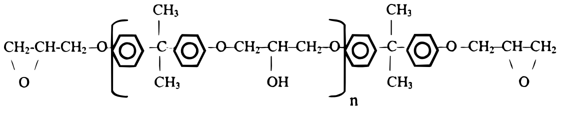
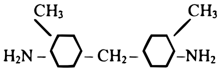
The polyepoxide precursors were a classical diepoxy prepolymer, diglycydyl ether of bisphenol A (DGEBA), with a low degree of polymerization ($n = 0.03$) and a cycloaliphatic diamine: 4,4′-diamino-3,3′-dimethyl dicyclohexyl methane (3DCM). The reactants were used as received with a stoichiometric ratio of epoxy to amino-hydrogen equal to unity.

The chemical structures and characteristics of the polymer and monomers are listed in Table 1.

For the blend preparation, the liquid diamine was added after complete dissolution of PVC in DGEBA at 130 °C. PVC is known to suffer degradation when treated in solution at high temperatures and, in particular, when strong bases such as aliphatic amines are present. The mixing and dissolution time was then reduced as much as possible preventing PVC degradation from occurring. The concentration of PVC in the solution will be expressed either as mass fraction, c, or volume fraction, ϕ.

3.2. Kinetic Studies. Kinetic studies were conducted in a regulated oil bath at various temperatures. Samples, placed in culture tubes, were removed from the bath after selected time intervals and studied by dissolution experiments and differential scanning calorimetry (DSC).[20]

Table 1. Structure and Characteristics of the Blend Components

Blend components	Formulae	Supplier	M (g/mol.$^{-1}$)	Tg (°C)
diglycidyl ether of bisphenol A (DGEBA) $\bar{n}$ = 0.03		Dow Chemical	348.5	/
4,4'-diamino-3,3'-dimethyl dicyclohexylmethane (3DCM)		BASF	238	/
poly(vinyl chloride) (PVC)	$\{CH_2-CHCl\}$	Elf Atochem	$\overline{M}_n$ = 44000 $\overline{M}_w$ = 88000	80

The chemical gelation time, t_{cg} was measured as the time at which the presence of an insoluble fraction in THF was first observed.

DSC analysis was carried out in a Mettler TA3000 apparatus under an argon atmosphere. Measurements of the glass transition temperature, T_g were conducted at a heating rate of 10 °C·min^{-1}. The epoxy–diamine vitrification time, t_{vitr} conceptually corresponds to the time at which the glass transition temperature of the reacting system, T_g reaches the cure temperature, T_i. t_{vitr} was experimentally defined as the time at which an exothermic physical aging peak appeared.

The resulting values of t_{cg} and t_{vitr} measured at different T_i were used to built on a TTT diagram the chemical gelation curve and the vitrification curve of the epoxy–diamine system, respectively.

Both the high reactivity of the 3DCM cycloaliphatic diamine and the low-temperature range used here ($T_i \leq 120$ °C) were found to prohibit the occurrence of any PVC degradation (no coloration of the samples) until t_{vitr} regardless of T_i.

3.3. Dynamic Mechanical Spectroscopy. The dynamic mechanical spectra of reactive blends were recorded at various temperatures in a frequency range from 10 to 100 rad/s using a Rheometrics Dynamic analyzer (RSA II) equipped with parallel plates. The plate diameter and the sample thickness were 25 and 1.5 mm, respectively. During the whole isothermal cure process, the shear amplitude was adjusted to give enough signal while ensuring the linearity of the dynamic viscoelasticity.

The rheological measurements performed here were limited due to compliance effects caused by the onset of vitrification of the epoxy–diamine copolymer, i.e., soon after the typical frequency-dependent tan δ maximum. To investigate the entire vitrification process, and in particular to observe the G'' maximum, a smaller diameter plate should be used. The disadvantage of this was that the rheometer was then unable to take accurate measurements during the early stages of cure. However, the aim of these rheological studies was not to accurately determine the vitrification time, t_{vitr}. Kinetic studies were performed for that. The frequency-dependent tan δ maximum was only used here to locate the vitrification zone with respect to other rheological events.

3.4. Light Transmission. A light transmission setup using visible light was used to investigate any liquid–liquid demixing process during isothermal cure of the blends. The liquid–liquid demixing time, t_{ll}, was determined as the onset time where a decrease in the transmitted light intensity was recorded.

3.5. Transmission Electron Microscopy. Electron microscopy was used to obtain images of the cured blends. Ultrathin sections were prepared at room temperature. Samples were imaged in a JEM-200CX transmission electron microscope with an accelerating voltage of 80 kV.

4. Results and Discussion

4.1. Initial Solubility of PVC in Epoxy and Reactive Epoxy–Diamine Solvents. Moderately concentrated PVC–DGEBA blends were observed to dissolve completely in a tube when stirred at 130 °C. Upon cooling of these nonreactive homogeneous solutions to room temperature, no liquid–liquid-phase separation occurred. Alternatively, physical gelation corresponding to liquid–solid demixing could be visually detected during isothermal aging by observing the typical cessation of liquid flow when the tube was tilted.

The diamine was added at 130 °C after complete dissolution of PVC in DGEBA. As a result of rapid cooling, limiting any further epoxy–diamine reaction, the reactive solution was found to behave similarly to the DGEBA–PVC system: only liquid–solid demixing took place, leading to the formation of physical gels as well. It is important to note that the cessation of liquid flow observed after short physical aging times at room temperature could be unambiguously attributed to physical gelation because neither chemical gelation nor vitrification of the growing epoxy–amine copolymer have occurred. This is because the samples were still completely soluble in THF and the vitrification time of the neat DGEBA–3DCM system is longer than 1 day at room temperature. Thus, on the basis of these solubility results, PVC–(DGEBA–3DCM) solutions can be considered as novel systems with regard to their ability to form chemically reactive physical gels.

The glass transition temperatures of the unreacted DGEBA–3DCM mixture and of the resulting fully cured chemical network are $T_{g0} = -32$ °C and $T_{g\infty} = 180$ °C, respectively.[20] The critical temperature at which chemical gelation and vitrification occur simultaneously in this system is ${}_{cg}T_g = 55$ °C,[20] affording a broad cure temperature range with which to reach chemical gelation.

The importance of the choice of the diamine needs to be emphasized since it was found to greatly influence the solvent suitability, as already reported in the literature[50,51] for different thermoplastic–thermoset precursors blends. For example, it was found here that PVC macroscopically precipitated after the addition of 4,4′-diaminodiphenyl sulfone or 4,4′-methylenedianiline, while chemically reactive physical gels could be achieved using 4,4′-methylenebis(3-chloro-2,6-diethylaniline).

Table 2. Liquid−Liquid Demixing Time, t_{ll} (s), Measured by Light Transmission, as a Function of Curing Temperature, T_i for the PVC−(DGEBA−3DCM) Solution with $c = 3.25$ %

T_i (°C)	120	115	110	105	100	95	90	≤85
t_{ll} (s)	165	217	258	295	340	469	669	no

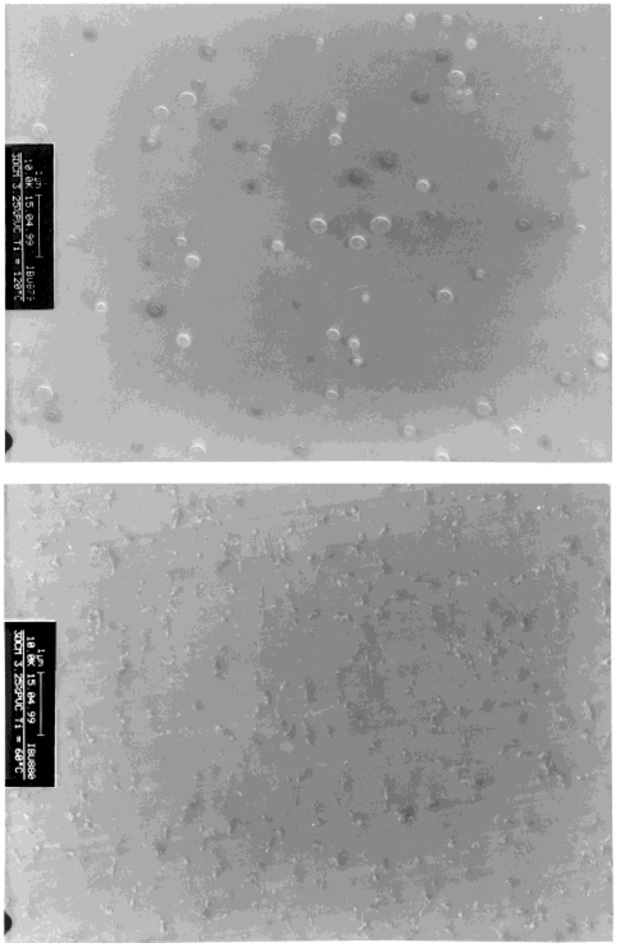


Figure 1. Transmission electron micrographs of the PVC−(DGEBA−3DCM) with $c = 3.25\%$: (a) $T_i = 120$ °C and curing time $t_i > t_{vitr}$; (b) $T_i = 70$ °C and curing time $t_i > t_{vitr}$.

4.2. Effect of Temperature on the Isothermal Behavior of Reactive PVC−(Epoxy−Diamine) Solutions. Homogeneous and low-concentrated PVC solutions in epoxy−diamine were quenched and then isothermally aged at various temperatures, T_i. The PVC concentration was first fixed to $c = 3.25\%$ since such a concentration was found to lead to experimentally convenient time scales of physical and/or chemical gelation over a wide temperature range. At such a low concentration, the dilution effect of reactive functional groups induced by the presence of PVC chains is not significant, and the temperature dependency of the epoxy−diamine reaction rate is therefore practically the same as that of the neat system.[50] Cure temperatures of interest are obviously located below the melting temperature, T_m, of any aged physical gel. Unfortunately, the determination of T_m is not possible for PVC−(epoxy−diamine) systems due to the unavoidable increase of the extent of reaction when the temperature is increased. Nevertheless, the temperatures used here were restricted to less than 120 °C with regard to known literature values of T_m for classical PVC gels.[18,35]

The changes in optical properties were monitored during isothermal cure of the initially homogeneous PVC−(DGEBA−3DCM) solutions using light transmission. The resulting liquid−liquid demixing times, t_{ll} are listed in Table 2 as a function of temperature.

For T_i equal or higher than 90 °C and for times well before chemical gelation, reaction-induced phase separation occurred, preventing the macroscopic physical gelation of PVC chains and leading to heterogeneous structures. The higher the T_i, the better the initial miscibility and therefore the higher the extent of reactions at phase separation, x_{ll}. Also, the higher T_i, the lower t_{ll} due to the chemical rate constants displaying Arrhenius-type behavior. The investigated PVC concentration is much lower than $c_{crit} = 6.55\%$ (see Appendix), thus predicting that the reaction-induced liquid−liquid demixing will generate a dispersion of PVC-rich particles in a continuous epoxy-rich matrix. This is highlighted by the micrograph in Figure 1a ($T_i = 120$ °C and $t_i > t_{vitr}$), which exhibits dispersed spherical domains corresponding to the PVC-rich phase.

Alternatively, for T_i equal or lower than 85 °C, no reaction-induced liquid−liquid demixing could be detected by light transmission, and the fully reacted samples remained clear.

To further investigate transformations occurring during isothermal cure of PVC−(DGEBA−3DCM) solutions for $T_i \leq 85$ °C, the dynamic viscoelastic properties were recorded as a function of time. Figures 2 and 3 present a multifrequency plot of loss tangent, tan δ vs time for $T_i = 50$ °C and $T_i = 70$ °C, respectively. Chemical gelation of the epoxy−diamine system was independently determined by using dissolution measurements and the resulting chemical gel times, t_{cg} are located on the time scale of both plots. After a short cure time of 370 s for $T_i = 50$ °C and 1300 s for $T_i = 70$ °C, well before t_{cg}, a crossover of tan δ curves is detected denoting the physical gelation time, t_{pg} of PVC chains in the growing epoxy−diamine copolymer. This result formalizes previous solubility discussions, based on the observation of the cessation of liquid flow, in the way that a macroscopic PVC physical gel swollen by the reacting DGEBA−3DCM solvent can actually be achieved at low temperature. Despite the thermodynamic instability of the system resulting from the further extent of polycondensation reactions, a macroscopic PVC gel structure is preserved and liquid−liquid demixing is limited to the finite PVC molecules of the sol fraction. This liquid−liquid phase separation is unlikely to produce dispersed PVC-rich particles, since the growth of the preexisting PVC gel is thermodynamically more favorable. The corresponding phase separation time, $t_{ll,sol}$ may correspond to the maximum of the tan δ curves observed around 6000 s for $T_i = 50$ °C and 1700 s for $T_i = 70$ °C. Such a maximum in tan δ has previously been observed for thermoplastic−epoxy blends at phase separation.[58] It is believed to originate from interfacial deformation of the newly formed interface between the developing phases.[59] In this sense, it would be a shape relaxation as opposed to molecular relaxations. This phenomenon is currently under study at our lab to validate this interpretation. At $t_{cg} = 10\,300$ s for $T_i = 50$ °C and 2100 s for $T_i = 70$ °C, macroscopic chemical gelation of the reactive solvent is isothermally reached without any singularity on the multifrequency plot, since a macroscopic physical gel already existed. Last, the frequency-dependent relaxation around 9000 s for

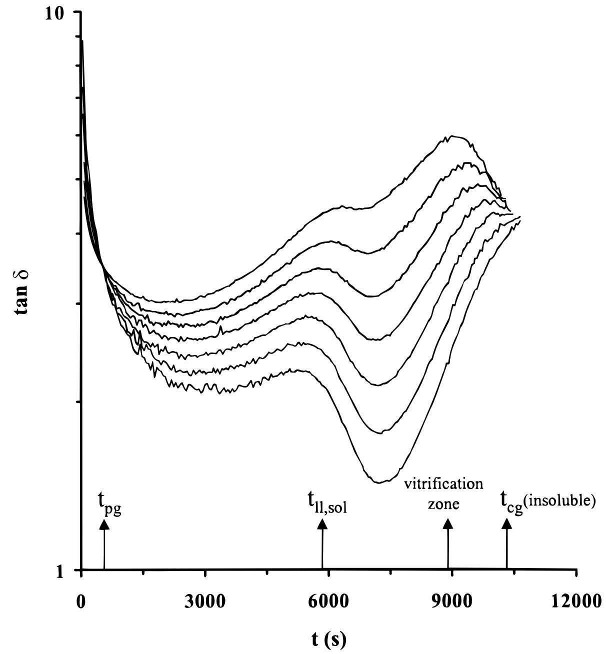


Figure 2. Loss tangent, tan δ, as a function of curing time for the PVC−(DGEBA−3DCM) with $c = 3.25\%$ at $T_i = 50$ °C and various angular frequencies (above t_{pg}, from top to bottom, $\omega = 10, 14.7, 21.5, 31.6, 46.4, 68.1, 100$ rad/s). t_{pg}, $t_{ll,sol}$, and t_{cg} denote the physical gelation, liquid−liquid demixing of PVC chains in the sol fraction, and chemical gelation time (insoluble), respectively.

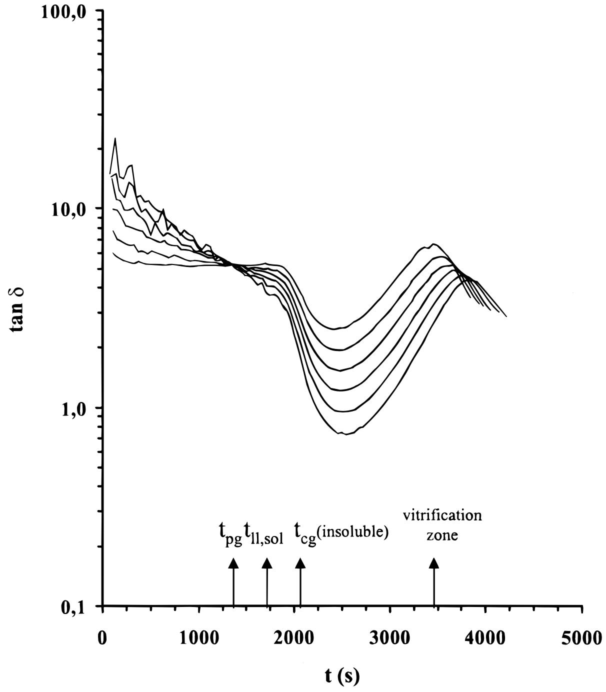


Figure 3. Loss tangent, tan δ as a function of curing time for the PVC−(DGEBA−3DCM) with $c = 3.25\%$ at $T_i = 70$ °C and various angular frequencies (above t_{pg}, from top to bottom, $\omega = 10, 15.8, 25.1, 39.8, 69.1, 100$ rad/s). t_{pg}, $t_{ll,sol}$, and t_{cg} denote the physical gelation, liquid−liquid demixing of PVC chains in the sol fraction and chemical gelation time (insoluble), respectively.

$T_i = 50$ °C and 3400 s for $T_i = 70$ °C exhibits behavior typical of vitrification for the growing epoxy−diamine copolymer. When $T_i = 50$ °C, vitrification is found to occur just before chemical gelation since that cure temperature is slightly lower than ${}_{cg}T_g$.

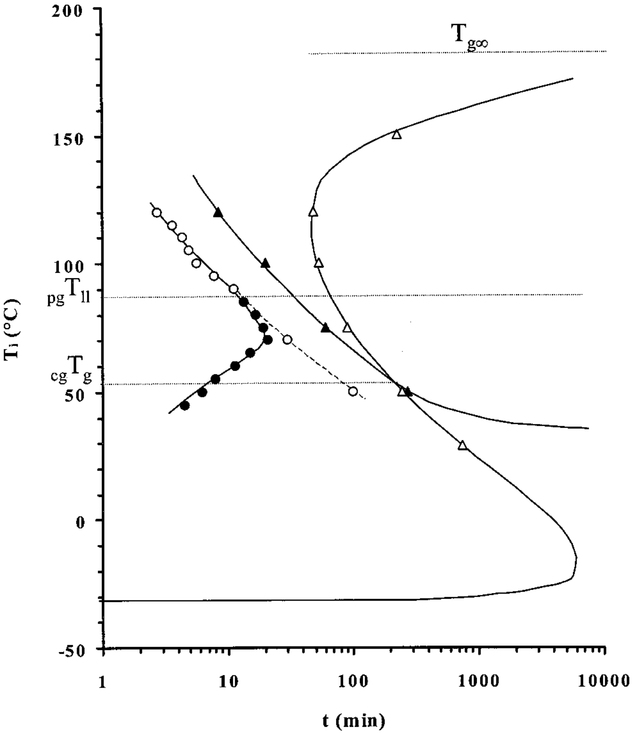


Figure 4. Time−temperature−transformation (TTT) diagram for PVC−(DGEBA−3DCM) with $c = 3.25\%$. Key: (−▲−) chemical gelation time, t_{cg} from kinetic studies; (−△−) thermoset vitrification time, t_{vitr} from kinetic studies; (−○−) liquid−liquid demixing time, t_{ll}, from light transmission; (---○---) liquid−liquid demixing time of PVC chains in the sol fraction, $t_{ll,sol}$ from the maximum of the tan δ curves; (−●−) physical gelation time, t_{pg} from the crossover of the tan δ curves. ${}_{pg}T_{ll}$ denotes the temperature at which physical gelation and liquid−liquid demixing occur simultaneously. The gray region corresponds to the temperature range for which interpenetrating chemical and physical gels are generated.

The main conclusion from this is that isothermal cure of PVC−(DGEBA−3DCM) at 50 or 70 °C does result in the build-up of true interpenetrating chemical and physical gels. Such a structure is clearly evidenced by the micrograph shown in Figure 1b ($T_i = 70$ °C and $t_i > t_{vitr}$), which shows the image of a percolating PVC structure in the two-dimension space.

Physical gelation times, t_{pg}, were more widely measured by dynamic viscoelasticity at a different T_i every 5 °C. The results are conveniently displayed on a TTT diagram (Figure 4), including besides (i) the chemical gelation curve, (ii) the vitrification curve of the epoxy−diamine system and (iii) the liquid−liquid demixing curve. The values of t_{cg} and t_{vitr} at different T_i used to build the chemical gelation curve and the vitrification curve were obtained from previous kinetic studies.[20] Such a TTT diagram summarizes all isothermal transformations occurring with time for the whole temperature range between T_{g0} and $T_{g\infty}$. First, it can be observed that the experimental times, corresponding to the first maximum of the tan δ curves after their crossover at $T_i = 50$ °C and $T_i = 70$ °C (Figures 2 and 3), lie in the continuity of the liquid−liquid demixing curve, built from light transmission measurements. This strengthens the idea that such maxima do in fact denote the liquid−liquid demixing time of PVC chains in the sol fraction, $t_{ll,sol}$. Second, the physical gelation curve (the evolution of t_{pg} with temperature will be discussed later) can be seen to meet the liquid−liquid demixing curve.

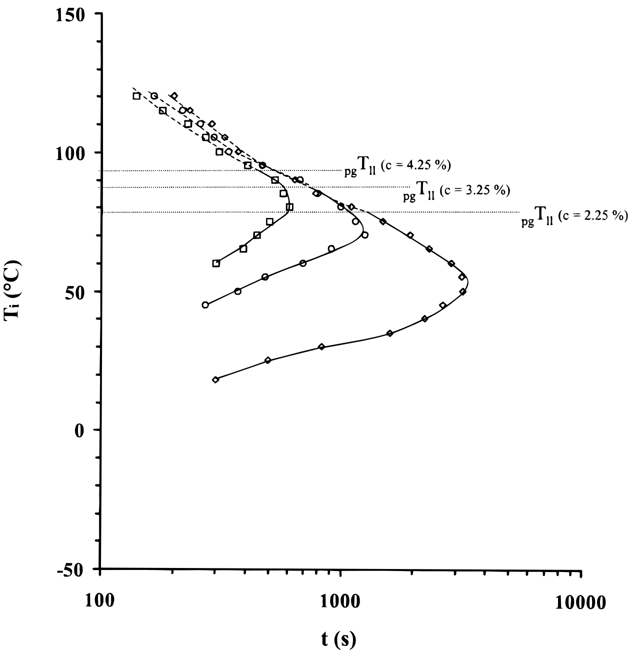


Figure 5. (- - -) Liquid−liquid demixing curve and (—) physical gelation curve for the PVC−(DGEBA−3DCM) with (◊) c = 2.25%, (○) c = 3.25%, and (□) c = 4.25%.

The behavior of this PVC−(epoxy−diamine) system is then clearly governed by the competition between the physical gelation rate and the reaction-induced phase separation rate. That competition leads to the definition of a novel temperature, $_{pg}T_{ll}$ denoting the temperature at which PVC physical gelation, pg, and liquid−liquid demixing, ll, occur simultaneously.

When $T_i > {}_{pg}T_{ll}$, the combination of a high epoxy−diamine reaction rate and a moderate degree of undercooling provides a higher reaction-induced demixing rate compared to the PVC gelation rate. Hence, as a result of the decrease of the entropy of mixing of the epoxy−diamine component, liquid−liquid-phase separation occurs first, preventing the macroscopic PVC physical gelation from occurring. In that temperature range, the blend behaves like a classical amorphous thermoplastic−thermoset blend, and the final heterogeneous structure consists of PVC-rich particles dispersed in a polyepoxide-rich matrix.

Alternatively, when $T_i < {}_{pg}T_{ll}$, the physical gelation rate is high enough to ensure the formation of a macroscopic PVC gel before any phase separation phenomenon. When the critical molar mass of the epoxy−diamine component is reached, a macroscopic "out of equilibrium" PVC gel structure is preserved, and liquid−liquid demixing is limited to the finite PVC molecules of the sol fraction, resulting in the growth of the physical gel. If the system is cured long enough equal or below $_{pg}T_{ll}$ (but above $_{cg}T_g$) to reach isothermally chemical gelation, true interpenetrating chemical (polyepoxide) and physical (PVC) gels are generated (gray region on the TTT diagram).

4.3. Concentration Dependence of $_{pg}T_{ll}$. The physical gelation curves and the liquid−liquid demixing curves were experimentally determined for two other PVC concentrations, c = 2.25% and c = 4.25%. All the results are displayed on a TTT diagram in Figure 5.

The lack of variation of t_{ll} with concentration is explained by the fact that (i) x_{ll} is relatively unaffected by the PVC concentration in the small range investigated and (ii) the dilution effect of reactive functional groups induced by the presence of PVC chains causes very limited variations in reaction times when the additive concentration is ranging from c = 2.25% to c = 4.25%.

On the other hand, a slight variation of concentration induces large variations in the physical gelation time. This is consistent with the strong scaling law dependence of the physical gelation rate, t_{pg}^{-1} with $(c - c_{pg})/c_{pg}$ (where c_{pg} is the critical PVC concentration that is necessary to form a physical gel) reported for crystallization-induced gels in nonreactive solvents.[45−49] Indeed, in good agreement with the presence of multiple junctions combining more than two polymer chains, a power law exponent close to 3 has been determined for PVC gels in di(2-ethylhexyl) phthalate (DOP).[45]

Finally, this shows that the variation of $_{pg}T_{ll}$, the intersection between t_{ll} and t_{pg}, with PVC concentration is mainly governed by the concentration-dependent function of the physical gelation rate, thus resulting in a shift of $_{pg}T_{ll}$ to higher temperatures when the initial PVC concentration is increased.

4.4. Temperature and Extent of Reaction Dependences of the Physical Gelation Rate, t_{pg}^{-1}. For crystallization-induced gels in nonreactive solvents, the physical gelation rate shows a temperature dependence similar to the nucleation rate of semicrystalline polymers in dilute solutions, resulting in[46−49]

$$\log t_{pg}^{-1} \propto T_m^{2}/T_i(\Delta T)^2 \qquad (2)$$

where T_m denotes the melting temperature of the crystalline phase in the solution and ΔT the undercooling ($T_m - T_i$). The physical gelation time then strongly increases when the degree of undercooling from the melt state decreases; i.e., the aging temperature increases.

While the TTT (T vs log t) representation is inadequate to discuss the variations of the physical gelation time/rate, an unusual behavior compared to nonreactive physically gelling solutions can be noted from Figures 4 and 5. Instead of monotonically increasing with temperature, t_{pg} actually passes through a maximum before decreasing until $_{pg}T_{ll}$ is reached.

Figure 6 shows the fitting of eq 2 to the experimental points for PVC solutions with c = 2.25%, 3.25%, and 4.25%. The indeterminable value of T_m was assigned a realistic value of 120 °C with regard to available literature values for classical PVC gels in that low concentration range. However, the choice of any melting temperature between 110 and 140 °C was found to not significantly affect the shape of the curves regardless of the concentration.

The experimental data are intrinsically limited (i) in the high-temperature region by $_{pg}T_{ll}$ and (ii) in the low-temperature region by an estimated temperature, T_{low} for which the time scale of physical gelation becomes comparable with the time scale of the mixing and measurement. At a given temperature, small decreases in the PVC concentration has been shown to greatly increase the physical gelation time. Also, slightly decreasing the PVC concentration significantly decreases T_{low} ($T_{low,c=4.25\%} \approx$ 60 °C, $T_{low,c=3.25\%} \approx$ 45 °C and $T_{low,c=2.25\%} \approx$ 15 °C), thus extending the possibility of t_{pg} measurements to lower temperatures because of the lower reactivity of the DGEBA−3DCM system and the enhancement of the physical gelation process caused by a greater degree of undercooling.

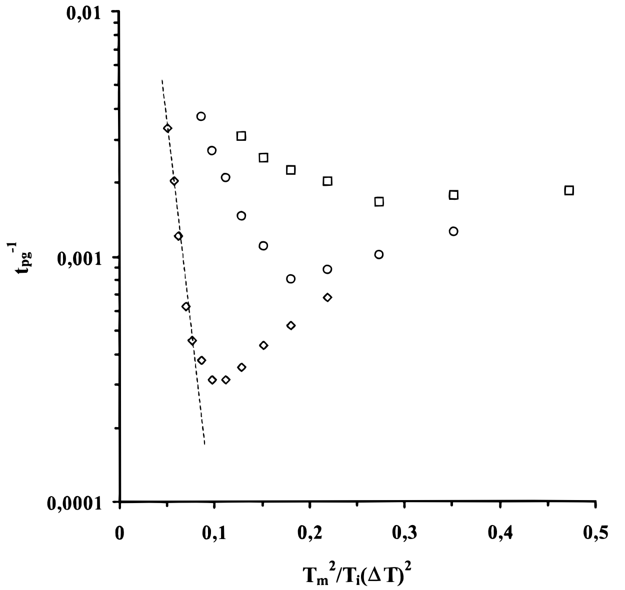


Figure 6. Physical gelation rate, t_{pg}^{-1} vs $T_m^2/T_i(\Delta T)^2$ for the PVC−(DGEBA−3DCM) with (◇) $c = 2.25\%$, (○) $c = 3.25\%$, (□) $c = 4.25\%$.

As long as the concentration/temperature conditions prevent the advancement of chemical reactions from being significant at the time where the physical gel is formed ($c = 2.25\%$ and $T_i < 30$ °C), a linear decrease of log t_{pg}^{-1} is observed as a function of $T_m^2/T_i(\Delta T)^2$ and the (DGEBA−3DCM)−PVC solutions behave like nonreactive crystallization-induced gelling systems.

Conversely, when the concentration/temperature conditions result in a significant extent of reactions at t_{pg} ($c = 2.25\%$ and $T_i > 30$ °C; $c = 3.25\%$ or 4.25% and $T_i > T_{low}$), eq 2 is no longer followed. The physical gelation rate for a given concentration becomes a complex function dependent on both temperature and the extent of the epoxy−diamine reaction.Whatever the PVC concentration, chemical reactions induce a decrease in the physical gelation time. The extent of chemical reaction made the epoxy−diamine a progressively poorer solvent thus accelerating the liquid−solid demixing process, i.e., the rate of crystallization of PVC. By increasing the temperature, a minimum gelation rate (a maximum t_{pg}) is observed, meaning that the advancement of reaction becomes the prevailing driving force for physical gelation compared to the initial quench depth from the melt state which governs the gelation rate of nonreactive physically gelling systems.

5. Conclusion

Low-concentrated solutions of PVC in epoxy−diamine monomers were observed to have the ability to form chemically reactive physical gels. The isothermal behavior of these solutions is governed by the competition between physical gelation rate and reaction-induced phase separation rate. The temperature, ${}_{pg}T_{ll}$, increasing with PVC concentration and denoting the temperature at which physical gelation and liquid−liquid demixing occur simultaneously, was then used to describe the versatility of these systems for a given PVC concentration:

(i) When $T_i > {}_{pg}T_{ll}$, the combination of a high epoxy−diamine reaction rate and a moderate degree of undercooling provides a higher reaction-induced demixing rate compared to the PVC gelation rate. In that temperature range, the blend definitively behaves like a classical amorphous thermoplastic−thermoset blend, and the final heterogeneous structure consists of PVC-rich particles dispersed in a polyepoxide-rich matrix.

(ii) When $T_i < {}_{pg}T_{ll}$, the physical gelation rate is high enough to ensure the formation of a macroscopic PVC gel before any phase separation phenomenon. When the critical molar mass of the epoxy−diamine component is reached, a macroscopic “out of equilibrium” PVC gel structure is preserved and liquid−liquid demixing is limited to the finite PVC molecules of the sol fraction, resulting in the growth of the physical gel. If the system is cured long enough equal or below ${}_{pg}T_{ll}$ (but above ${}_{cg}T_g$) to reach isothermally chemical gelation, true interpenetrating chemical (polyepoxide) and physical (PVC) gels are generated and the ultimate materials are clear.

The usual temperature-dependent function of the crystallization-induced physical gelation rate was found to be affected by the extent of epoxy−diamine polycondensation reactions. Chemical reactions made the epoxy−diamine solvent to become progressively poorer, thus accelerating the liquid−solid demixing process, i.e., the rate of crystallization of PVC, and resulting in a decrease of the physical gelation time compared to nonreactive physically gelling systems.

Beside their originality, interpenetrating chemical (polyepoxide) and physical (PVC) gels can be expected to exhibit very specific and attractive properties. For instance, these systems may constitute an interesting alternative to increase the fracture toughness of polyepoxide networks. Taking advantage of both the presence of a percolating thermoplastic structure for low concentrations and the conductivity of PVC chains after controlled degradation, a polyepoxide material with conductive properties may also be imagined. Another potential application is to use the thermoreversibility of a physical gel based on a blocked (nonreactive) thermoset precursor at room temperature to control the initial viscosity and the processability of coating formulations. Work is now in progress to investigate such properties.

The concept of interpenetrating chemical and physical gels may also be more widely extended to other semicrystalline thermoplastics (PVDF, syndiotactic PS, ...) with the ability to form physical gels in solution, providing appropriate reactive solvents can be found. It may be also extended to physically gelling systems in which junctions are no longer crystalline regions but hydrogen bonds, ionic clusters, or phase-separated microdomains.

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Appendix: Calculation of the Critical Concentration for the PVC−(DGEBA−3DCM) Blend

From the classical Flory−Huggins model applied to a quasi-binary blend of a polydisperse thermoplastic in the thermoset precursors, the volume fraction of thermoplastic at the critical point, ϕ_{crit} may be expressed as[53,57]

$$1/\phi_{\text{crit}} = 1 + (V_{\text{TP}}/V_{\text{TS}})^{1/2} x_{\text{w}}(\text{TP})/[x_z(\text{TP})]^{1/2} \qquad \text{(A-1)}$$

where V_{TP} is the molar volume of the constitutional repeating unit of the thermoplastic polymer, V_{TS} is the molar volume of the thermoset precursors taken as a single pseudomonomer, and $x_{\text{w}}(\text{TP})$ and $x_z(\text{TP})$ are the w- and *z*-average degrees of polymerization of the polydisperse thermoplastic, respectively. To determine the value of ϕ_{crit} from eq A-1, the value of $x_z(\text{TP})$ has to be estimated by assuming a particular distribution of molar masses.

To estimate the value of $x_z(\text{PVC})$, the Schulz-Zimm distribution[60] was used

$$x_{\text{n}}(\text{TP}) = h/g; \quad x_{\text{w}}(\text{TP})/x_{\text{n}}(\text{TP}) = (1 + h)/h; \quad x_z(\text{TP})/x_{\text{w}}(\text{TP}) = (2 + h)/(1 + h) \qquad \text{(A-2)}$$

where *h* and *g* are the parameters that characterize the distribution of molar masses.

Estimating the value of $x_z(\text{PVC})$ from eq A-2 and replacing it into eq A-1 led to $\phi_{\text{crit}} = 0.059$ or $c_{\text{crit}} = 6.55\%$.

References and Notes

(1) Stauffer, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1354.
(2) De Gennes, P. G. *J. Phys. (Paris)* **1976**, *L1*, 37.
(3) Chambon, F.; Winter, H. H. *J. Rheol.* **1986**, *30*, 367.
(4) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683.
(5) Durand, D.; Delsanti, M.; Adam, M.; Luck, T. M. *Europhys. Lett.* **1987**, *3*, 277.
(6) Adolf, D.; Martin, J. E. *Macromolecules* **1990**, *23*, 3700.
(7) Adolf, D.; Martin, J. E.; Wilcoxon, J. P. *Macromolecules* **1990**, *23*, 527.
(8) Hodgson, D. F.; Amis, E. J. *Macromolecules* **1990**, *23*, 2512.
(9) Scanlan, J. C.; Winter, H. H. *Makomol. Chem., Macromol. Symp.* **1991**, *45*, 11.
(10) Lairez, D.; Adam, M.; Emery, J. R.; Durand, D. *Macromolecules* **1992**, *25*, 286.
(11) Devreux, F.; Boilot, J. P.; Chaput, F.; Malier, L.; Axelos, M. A. V. *Phys. Rev.* **1993**, *47*, 2689.
(12) Miaoling, L. H.; Williams, J. G. *Macromolecules* **1994**, *27*, 7426.
(13) Eloundou, J. P.; Feve, M.; Gerard, J. F.; Harran, D.; Pascault, J. P. *Macromolecules* **1996**, *29*, 6907.
(14) Te Nijenhuis, K.; Winter, H. H. *Macromolecules* **1989**, *22*, 411.
(15) Li, L.; Aoki, Y. *Macromolecules* **1997**, *30*, 7835.
(16) Watanabe, H.; Sato, T.; Osaki, K.; Aoki, Y.; Li, L.; Kakiuchi, M.; Yao, M. L. *Macromolecules* **1998**, *31*, 4198.
(17) Aoki, Y.; Uchida, H.; Kakiuchi, M. *Macromolecules* **1998**, *31*, 7472.
(18) Aoki, Y.; Li, L.; Kakiuchi, M. *Macromolecules* **1998**, *31*, 8117.
(19) Grillet, A. C.; Galy, J.; Pascault, J. P.; Bardin, I. *Polymer* **1989**, *30*, 2094.
(20) Verchère, D.; Sautereau, H.; Pascault, J. P.; Riccardi, C. C.; Moschiar, S. M.; Williams, R. J. J. *Macromolecules* **1990**, *23*, 725.
(21) Girard-Reydet, E.; Riccardi, C. C.; Sautereau, H.; Pascault, J. P. *Macromolecules* **1995**, *28*, 7599.
(22) Horie, K.; Hiura, H.; Sauvada, M.; Mika, I.; Kambe, H. *J. Polym. Sci.—Polym. Chem.* **1970**, *8*, 1357.
(23) Dusek, K.; Ilavsky, M.; Lunak, S. *J. Polym. Sci.—Polym. Symp.* **1975**, *53*, 29.
(24) Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. J. *J. Appl. Polym. Sci.* **1984**, *29*, 2481.
(25) Havlicek, I.; Dusek, K. In *Cross-linked Epoxies*, Sedlacek, B., Kahovec, J., Eds.; Walter de Gruyter: Berlin 1987; p 359.
(26) Simon, S. L.; Gillham, J. K. *J. Appl. Polym. Sci.* **1992**, *46*, 1245.
(27) Deng, Y.; Martin, C. *Macromolecules* **1994**, *27*, 5141.
(28) Macosko, C. W.; Miller, D. *Macromolecules* **1976**, *9*, 206.
(29) Dusek, K. *Adv. Polym. Sci.* **1986**, *78*, 1.
(30) Gillham, J. K. *J. Appl. Polym. Sci.* **1973**, *17*, 2067.
(31) Guerrero, S. J.; Keller, A. *J. Macromol. Sci.—Phys.* **1980**, *B20*, 167.
(32) Yang, Y. C.; Geil, P. H. *J. Macromol. Sci.—Phys.* **1983**, *B22*, 463.
(33) Mutin, P. H.; Guenet, J. M. *Macromolecules* **1989**, *22*, 843.
(34) Najeh, M.; Munch, J. P.; Guenet, J. M. *Macromolecules* **1992**, *25*, 7018.
(35) Guenet, J. M. In *Thermoreversible Gelation of Polymers and Biopolymers*; Academic Press: New York, 1992.
(36) Soenen, H.; Berghmans, H. *Polym. Gels Networks* **1994**, *2*, 159.
(37) Keller, A. *Faraday Discuss.* **1995**, *101*, 1.
(38) Soenen, H.; Berghmans, H. *J. Polym. Sci.—Polym. Phys.* **1996**, *34*, 241.
(39) Lopez, D.; Mijangos; C.; Munoz, M. E.; Santamaria, A. *Macromolecules* **1996**, 29, 7108.
(40) Reinecke, H.; Mijangos, C.; Brulet, A.; Guenet, J. M. *Macromolecules* **1997**, 30, 959.
(41) Dahmani, M.; Fazel, N.; Munch, J. P.; Guenet, J. M. *Macromolecules* **1997**, *30*, 1463.
(42) Ross-Murphy, S. B. In *Polymer Gels*; DeRossi, D., Ed.; Plenum Press: New York, 1991; p 21.
(43) Stockmayer, W. H. *Macromolecules* **1991**, *24*, 6367.
(44) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943.
(45) Cloitre, M.; Girard-Reydet, E.; Leibler, L. To be submitted for publication.
(46) Okhura, M.; Kaniaya, T.; Kaji, K. *Polymer* **1992**, *33*, 5044.
(47) Mal, S.; Maiti, P.; Nandi, A. K. *Macromolecules* **1995**, *28*, 2371.
(48) Mal, S.; Nandi, A. K. *Polymer* **1998**, *39*, 6301.
(49) Dikshit, A. K.; Nandi, A. K. *Macromolecules* **1998**, *31*, 8886.
(50) Girard-Reydet, E.; Riccardi, C. C.; Sautereau, H.; Pascault, J. P. *Macromolecules* **1995**, *28*, 7608.
(51) Riccardi, C. C.; Borrajo, J.; Williams, R. J. J.; Girard-Reydet, E.; Sautereau, H.; Pascault, J. P. *J. Polym. Sci.—Polym. Phys.* **1996**, *34*, 349.
(52) Ohnaga, T.; Chen, W.; Inoue, T. *Polymer* **1994**, *35*, 3774.
(53) Clarke, N.; McLeish, T. C. B.; Jenkins, S. D. *Macromolecules* **1995**, *28*, 4650.
(54) Elliniadis, S.; Higgins, J. S.; Clarke, N.; McLeish, T. C. B.; Choudhery, R. A.; Jenkins, S. D. *Polymer* **1997**, 38, 4855.
(55) Elicabe, G. E.; Larrondo, H. A.; Williams R. J. J. *Macromolecules* **1997**, *30*, 6550.
(56) Girard-Reydet, E.; Sautereau, H.; Pascault, J. P.; Keates, P.; Navard, P.; Thollet, G.; Vigier, G. *Polymer* **1998**, *39*, 2269.
(57) Pascault, J. P.; Williams, R. J. J. In *Polymer Blends: Formulation and Performance*; Paul, D. R., Bucknall, C. B., Eds.; Wiley: New York, 2000.
(58) Vinh-Tung, C.; Lachenal, G.; Chabert, B.; Pascault, J. P. In *Toughened Plastics II: Novel Approaches in Science and Engineering*; Riew, C. K., Kinloch, A. J., Eds.; Advances in Chemistry 252; American Chemical Society: Washington, DC, 1994; p 59.
(59) Graebling, D.; Muller, R.; Palierne, J. F. *Macromolecules* **1993**, *26*, 320.
(60) Peebles, L. H. *Molecular Weight Distributions in Polymers*; Interscience: Wiley: New York, 1971.

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