Kinetics of Simultaneous Interpenetrating Polymer Networks of Poly(dimethylsiloxane–urethane)/Poly(methyl methacrylate) Formation and Studies of Their Phase Morphology

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ABSTRACT: Kinetics studies of simultaneous interpenetrating polymer networks (SIPNs) of poly(dimethylsiloxane–urethane) (PDMSU)/poly(methyl methacrylate) (PMMA) have been carried out by means of differential scanning calorimetry (DSC) with computer-aided DSC data analysis programs. The kinetic parameters such as conversion versus time and temperature, heat of reaction ΔH, activation energy ΔE, and reaction order n have been investigated by DSC isothermal and scanning modes. The experimental evidence clearly showed that the phase morphology of the SIPN of PDMSU/PMMA was changed by changing rates of their cross-linking reactions. A miscible IPN with 80 wt % PDMSU made with well-matched rates of cross-linking reactions in the network formation exhibited one glass transition temperature (T_g) and no SEM observable phase domains. However, an immiscible IPN with the same composition of PDMSU could be prepared with a much slower cross-linking reaction producing a phase-separated IPN with two T_gs from DSC measurements and a heterogeneous phase morphology observed by SEM.

Introduction

Interpenetrating polymer networks (IPNs) can be classified as novel polyblends held together predominantly by permanent entanglement of two or more cross-linked networks rather than covalent bond grafting.[1,2] Their physical properties, e.g., their mechanical behavior of the IPNs, depend on their phase morphology.[3,4] The simultaneous IPNs (SIPNs) phase morphology is affected by at least three factors. The first factor is the difference of the solubility parameters (δ) of the pure linear chain components. The smaller the difference, $\Delta\delta$, of the solubility parameters of the pure components, the smaller is the "thermodynamic" demixing tendency that produces either complete or microphase separation in the IPNs. The second factor is the magnitude of the chain mobilities of the IPN polymers which is associated with the T_gs of the polymers. In particular, if both T_gs are commensurate, there should be a smaller "dynamic" demixing tendency.[5]

In this paper we are mainly concerned with the third factor which is the match in kinetic rates of cross-linking of the individual networks producing gelation. In preparing a simultaneous IPN one attempts to approximately match the rates of the cross-linking reaction of the individual networks in order to get the maximum physical entanglement of the networks before "uphill" diffusion produces phase separation.[6] Some reports have indicated that the larger the difference in the rates of cross-linking of the networks, the less is the miscibility of the IPN components (the degree of segregation of the components in the IPN depended on the mismatch in the rate of formation of each of the networks). The tensile strength of the network reached a maximum when the component IPN networks gelled simultaneously.[7-10] FT-IR has been widely used for kinetics studies of simultaneous IPN formation. However, there are some disadvantages in studying SIPN formation by IR because of the instrument and sample preparation limitations. These factors are limitations produced by sample thickness, absorption peak overlap, and difficulties with temperature control, which lead sometimes to somewhat different kinetics reported by different investigations.[11-15] Differential scanning calorimetry (DSC) has been widely employed for thermal characterization of polymeric materials especially thermoset resins such as epoxy resin curing[16-18] and polyurethane (PU)/polyester SIPN which showed that the degree of cross-linking in each SIPN component had a significant effect on the dynamics of the SIPN formation.[19]

Recently the SIPNs of poly(dimethylsiloxane–urethane) (PDMSU)/poly(methyl methacrylate) (PMMA) were prepared and characterized in our laboratory.[20] The PDMSU was prepared by using new oligomers of bis[(β-hydroxyethoxy)methyl]poly(dimethylsiloxane) (PDMS-diol) and the new cross-linker tris[[(β-hydroxyethoxy)methyl]dimethylsiloxy]phenylsilane (Si-triol). Over the full composition range, the SIPNs of PDMSU/PMMA were totally phase separated, with phase domain sizes ranging from 0.2 to several micrometers. As previously suggested,[5] the difference in solubility parameters and T_gs may roughly correlate with the phase morphology of fully phase-separated PDMSU/PMMA IPNs (the calculated solubility parameters of linear PMMA δ = 9.2 cal/cm^3, PDMSU δ = 8.0 cal/cm^3, T_g(PMMA) = 105 °C, T_g(PDMSU) = -110 °C).[21]

However, this raised the question of whether the phase morphology of SIPNs of PDMSU/PMMA can be changed by changing the kinetics of network formation. In the next section, a direct experiment has been designed using a DSC with computer-aided DSC data analysis programs to monitor the cross-linking of the network formation of PDMSU/PMMA IPNs. The results from DSC kinetics measurements were fully consistent with those obtained from direct chemical experiment (gravimetry). The phase morphologies of the products prepared by us suggested by the DSC scans were confirmed by scanning electron microscopy (SEM). The experimental evidence clearly showed that the phase morphologies of the SIPNs can be changed by changing the gelation times of network formation. It was found that well-matched gelation times of the networks made the SIPNs more miscible; thus, even a SIPN of PDMSU/PMMA with a single T_g can be prepared. On the other hand, the totally phase-separated SIPN of PDMSU/PMMA can be formed if there is a larger difference of the gelation times of network formation. The

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Table 1. Raw Materials Employed and Their Abbreviation

designation	name and description	source
PDMS-diol	bis[(β-hydroxyethoxy)methyl]poly(dimethylsiloxane) M_W 940	Institute of Organo-elemento Compounds, Russian Academy of Sciences
Si-triol	tris[[(β-hydroxyethoxy)methyl]dimethylsiloxy]phenylsilane	Institute of Organo-elemento Compounds, Russian Academy of Sciences
BTI (Desmodur N-100)	biuret triisocyanate derived from hexamethylene diisocyanate, isocyanate functionality 2.62	Mobay Chem. Co.
MMA	methyl methacrylate	Aldrich Chem. Co.
EGDMA	ethylene glycol dimethacrylate	Aldrich Chem. Co.
BPO	benzoyl peroxide (97%)	Aldrich Chem. Co.
VAZO 52	2,2′-azobis(2,4-dimethylvaleronitrile)	DuPont Co.
HDI	hexamethylene diisocyanate (98%)	Aldrich Chem. Co.
petroleum ether	solvent grade	Aldrich Chem. Co.

DSC measurements were carried out immediately on preparation of the sample. Since the morphology of such macromolecular topological isomers can be chain mobility controlled, and these mobilities can be very small, one could find that such apparent single-phased materials become phase-separated on time scales on the order of years.[22,23]

Experimental Section

1. **Raw Materials.** Table 1 lists the raw materials employed in this paper. PDMS-diol and the cross-linker Si-triol were supplied by the Institute of Organoelemento Compounds of the Russian Academy of Sciences. The details of the synthesis of these oligomers and cross-linker are give in refs 24 and 25. The purification and treatment of all the chemicals used were described in ref 20 except the VAZO compound. VAZO 52 (2,2′-azobis(2,4-dimethylvaleronitrile)) was supplied by DuPont in a frozen, dry state and kept in a freezer. The synthesis of the SIPNs, blends of the linear components, and the pure cross-linked networks of PDMSU and PMMA are almost the same as those described in ref 20 except that VAZO 52 was used as an initiator without toluene as solvent. The molecular weights between cross-links (M_c) of PDMSU and PMMA are 1300 and 4000 separately from the employed raw material stoichiometry.

The formation of IPN (conversion) as a function of time was determined gravimetrically. Aliquots of the IPN polymerization were terminated at various time intervals by pouring them into a solution of petroleum ether with 0.1 wt % hydroquinone which was vigorously stirred for 4 h and precipitated overnight. The product was then washed several times with fresh methanol. The product IPN was then dried under vacuum at 80 °C for 48 h and then weighed. The conversion of the monomers was then calculated from this weight.

2. **Instrumental Methods and Procedures.** Differential scanning calorimetry (DSC; 2910 TA Instruments) was used to study the kinetics of the reactions involved in the SIPN formation. Computer-aided data analysis software programs for two kinds of DSC kinetics studies (the Borchardt/Daniels (B/D) method and isothermal kinetics) were provided by TA Instruments. The details of precise specifications of the methods and identification of the assumptions for the data analysis programs were described in the literature with a precision in the range of +5.0%.[26-28] The DSC kinetics studies of the SIPNs of PDMSU/PMMA used two modes. The first is the scanning mode which was based on the B/D method where the rate profile versus temperature was recorded. The second is the isothermal mode where the reaction exothermic rate versus time was followed. The base-line and cell constant of the DSC was calculated in accord with the DSC kinetic data analysis programs[27,28] before commencing the DSC kinetic studies.

Due to the volatile nature of methyl methacrylate (MMA) and HDI, all samples were prepared in a hermetically sealed pan (TA Instruments) to ensure that no significant mass loss occurs during reaction since the sample weight was assumed constant in the calculations. In the experiment the weight loss of the sample in the scanning mode (up to 200 °C) is less than 8%, and no weight loss was observed in the isothermal mode studies (at 50–80 °C). All ingredients were mixed with vigorous stirring, under a N_2 atmosphere, until a homogeneous solution was obtained. The typical procedure to make the solution is as follows: 0.40 g of PDMS-diol (M_W 940) was mixed with 0.16 g of Si-triol, then 0.20 g of MMA, and 20 mg of ethylene glycol dimethacrylate (EGDMA) cross-linker, and 5 mg of VAZO 52 initiator was added. The mixture was vigorously stirred until all chemicals dissolved completely; then 0.17 g of HDI was dropped into the solution under a N_2 atmosphere while vigorously stirring for 2 min. A clear solution was then obtained, and about 10–15 mg of sample was then transferred to the sample pan. The sample pan was washed with acetone and then air dried at 110 °C before use. A stream of dry N_2 was used to purge the O_2 and moisture that might have existed inside the sample holder, which was then sealed with the TA pressing machine under N_2. Due to the fast reaction rate of isocyanate with hydroxyl groups, the time required to make the solution (after adding HDI) until the start of the DSC measurements should be short (less than 5 min) in order that the DSC could record the entire reaction as completely as possible. The second scanning mode was conducted immediately following an isothermal or a scanning run from room temperature to 250 °C to ensure completeness of the cross-linking reactions.

Characterization. The studies of the phase morphology of the IPNs were carried out by means of DSC and SEM. If multiple T_gs and various phase domain sizes existed in the IPN, it was considered to be phase separated. The samples from the DSC isothermal mode were used to test their T_gs. DSC measurements were carried out between −150 and +200 °C at various scanning rates under a N_2 atmosphere. The first run was performed at a heating rate of 20 °C/min and was then cooled down at a rate of 20 °C/min, followed by heating at 40 °C/min. The same procedure was applied to the samples which were prepared by gravimetric experiment using the DSC isothermal mode condition.

SEM micrographs were taken on a digital scanning microscope (DSM 940; Zeiss, Germany). The specimens were frozen under liquid nitrogen, and they were then fractured and mounted on a stub using silver paint. Subsequently they were coated with gold (100 Å) on a Balzere SCD 004 sputter coater. The machine was operated at 15 kV, and the electron images were recorded directly from the cathode ray tube on Polaroid 55 film. The typical magnification employed was 10 000×.

Results and Discussion

1. **Scanning Mode (B/D Method).** Figure 1 gives the DSC traces of the chain polymerization of MMA monomer using VAZO and BPO as initiators at scanning rate of 5 °C/min. Three stages of the polymerization of MMA can be clearly seen from both traces. Stage I indicated the induction period because trace amounts of oxygen inhibited the reaction. Stage II showed the polymerization proceeding at a uniform rate. Stage III was caused by the Trommsdorff–Norrish effect. There is about 20 °C difference between the maxima in the heat evolution peaks due to the difference of the decomposition constant (K_d) of VAZO and BPO. (K_d(VAZO) = 1.9×10^{-4}/s at 68 °C, K_d(BPO) = 1.1×10^{-5}/s at 70.3 °C.[29]) The cross-linking reaction of PDMSU exhibited the typical step polymerization behavior as shown in Figure 2. The temperature range of the heat evolution in the formation of PDMSU occurred from 25 to 125 °C.

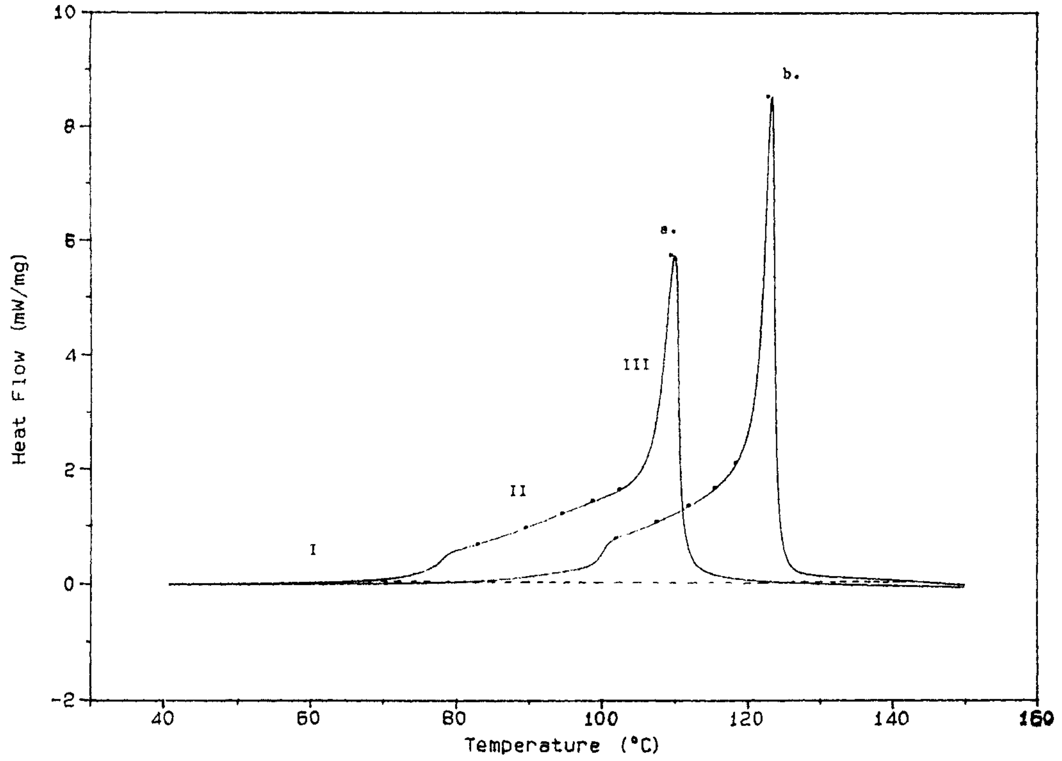


Figure 1. DSC traces of the polymerization of MMA monomer at a scanning rate of 5 °C/min: (a) VAZO 52 initiator; (b) BPO initiator.

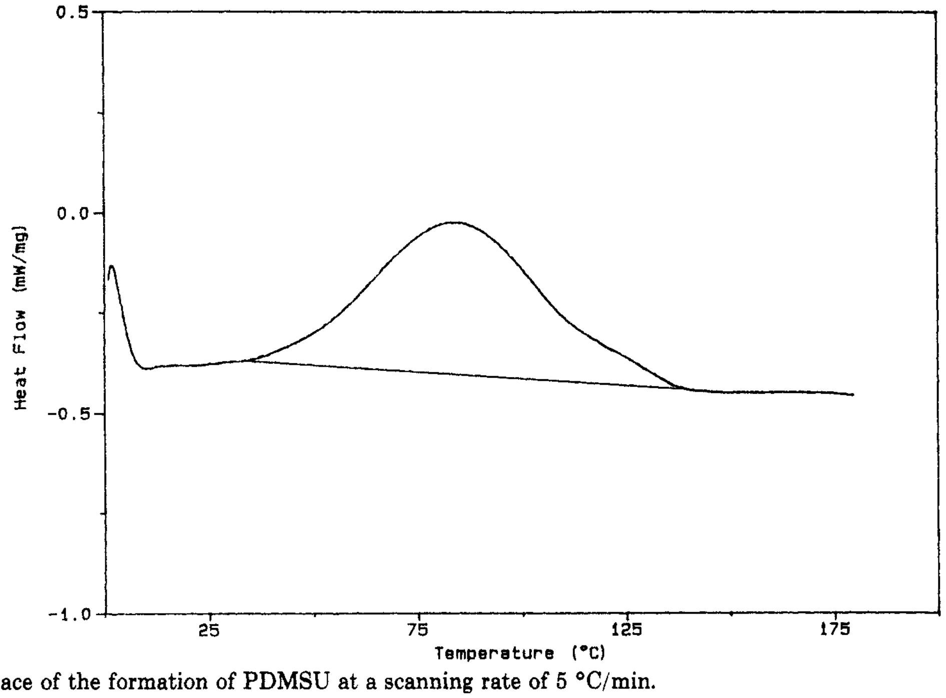


Figure 2. DSC trace of the formation of PDMSU at a scanning rate of 5 °C/min.

On the basis of the Borchardt and Daniels (B/D) assumption,[30] the reaction follows nth order kinetics, i.e.,

$$d\alpha/dt = -K(T)\,(1-\alpha)^n \tag{1}$$

with $d\alpha/dt$ the reaction rate (1/s) and α the fractional conversion, $K(T)$ is the specific rate constant at temperature T (1/s), and n is the reaction order. The B/D methodalso assumes that the temperature dependence of $K(T)$ follows the Arrhenius expression:

$$K(T) = Z\exp(-\Delta E/RT) \tag{2}$$

where Z is the preexponential factor (1/s), ΔE is the activation energy (J/mol), R is the gas constant (8.314 J/mol·K), and T is the absolute temperature (K). Taking logarithms to base e, eq 1 can be rewritten as

$$\mathrm{Ln}(d\alpha/dt) = \mathrm{Ln}\,Z - \Delta E/RT + n\,\mathrm{Ln}(1-\alpha) \tag{3}$$

The DSC exotherm is used to measure the two basic parameters $d\alpha/dt$ and α. The method assumes that the heat evolution in a small time interval is directly proportional to the number of moles reacted during that time. The reaction rate is obtained by dividing the rate of change of the peak height (dH/dt) at temperature T by the total heat of the reaction,

$$d\alpha/dt = (dH/dt)/\Delta H_0 \tag{4}$$

where ΔH_0 is the total peak area or the theoretical enthalpy. The fractional conversion is obtained by measuring the

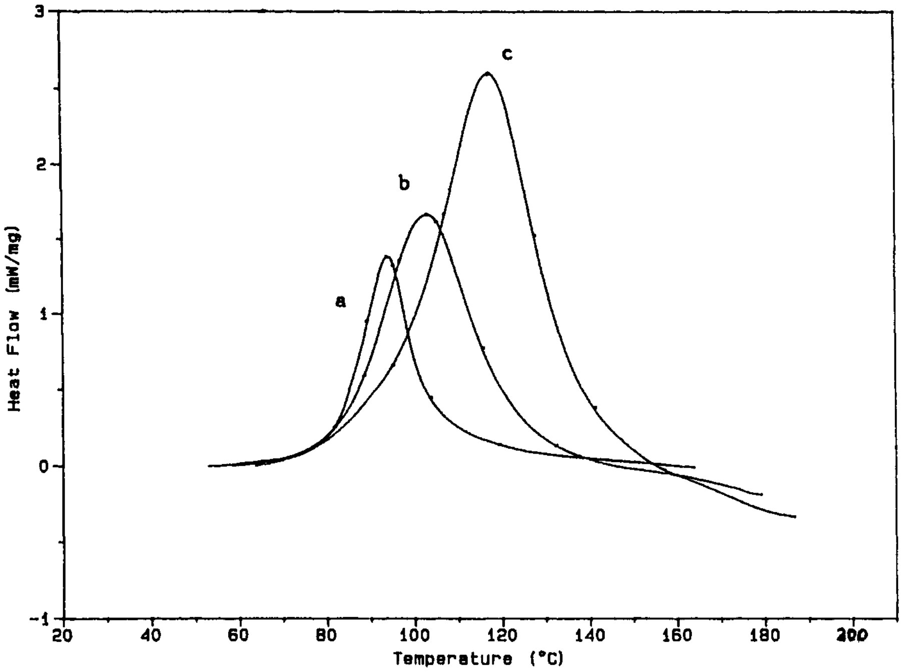


Figure 3. DSC traces of the formation of PDMSU/PMMA IPN (50% by weight PDMSU) at different scanning rates: (a) 5 °C/min; (b) 10 °C/min; (c) 20 °C/min. Note: M_c(PDMSU) = 1300; M_c(PMMA) = 4000.

ratio of the partial area, $\Delta H(T)$, at temperature T to the total peak area

$$a = \Delta H(T)/\Delta H_0 \qquad (5)$$

Using eqs 4 and 5 and the temperature and fractional conversion dependence, eq 3 can be solved to obtain n and ΔE.

The DSC kinetics studies via a computer-aided data analysis program (B/D method) showed a first-order reaction for the pure polymerization of MMA regardless of whether VAZO or BPO was used as an initiator. This is consistent with the result from FT-IR measurements.[11] The $\Delta E_{\mathrm{MMA/VAZO}}$ is less by about 20 kJ/mol than that of $\Delta E_{\mathrm{MMA/BPO}}$ ($\Delta E_{\mathrm{MMA/VAZO}}$ = 50.5 kJ/mol, $\Delta E_{\mathrm{MMA/BPO}}$ = 69.8 kJ/mol). The ΔHs for MMA/VAZO and MMA/BPO are 555.6 and 585.8 J/g, respectively, which are quite close to the literature value of ΔH_{PMMA} = 580 J/g.[28] The cross-linking reaction of PDMSU behaves as the second-order reaction which is similar to polyurethane (PU) formation.[31] The $\Delta H_{\mathrm{PDMSU}}$ is 110.7 J/g. The conversions with time and temperature of the polymerization of MMA using VAZO and BPO as initiator were also studied. The conversions of MMA are about 25% and 68% (wt) by using BPO and VAZO at 60 °C for 1 h and 30% and 65% (wt) at 70 °C for 0.5 h, respectively.

Figure 3 gives the curves of the formation of IPN of 50% (wt) PDMSU/PMMA at different scanning rates. The exothermal peak of the IPN formation became narrower and shifted to higher temperature compared to that of pure CPDMSU. This is possibly due to the dilution effect of MMA monomer. Increasing the scanning rate, the exothermal peak moved to a higher temperature but still maintained one peak. The total (measured) $\Delta H_{0,\mathrm{IPN}}$ = 315.8 J/g obtained from DSC scans is almost equal to $\Delta H'_{\mathrm{IPN}}$ (333 J/g) of the linear addition of ΔH_{PMMa} and $\Delta H_{\mathrm{PDMSU}}$ ($\Delta H'_{\mathrm{IPN}} = X\Delta H_{\mathrm{PMMA}} + (1 - X)\Delta H_{\mathrm{PDMSU}}$, X = wt % of PMMA). The overall reaction order n for the formation of the PDMSU/PMMA SIPN is 1.5 from the scanning mode at different scanning rates of 5 and 10 °C/min. This probably reflects a complex reaction mechanism. A similar kinetic result was reported in PU/PMMA IPN measured by FT-IR.[13] Decreasing the PDMSU amount resulted in an earlier onset of the Trommsdorff effect due to the extra heat of polymerization of the MMA monomer which helped to speed up the reaction of PDMSU. A similar phenomenon has been observed in several IPN systems.[8,12,32]

Figures 4 and 5 give the conversion versus time and temperature of the IPN formation based on DSC data analysis. A relatively higher conversion to the IPN can be found than that of the PMMA network. This is reasonable since the high initial conversion of the step polycondensation of PDMSU occurs initially and is then promoted by the heat released from the MMA polymerization.

2. Isothermal Mode. Isothermal mode analysis has also been performed on the kinetics of IPN formation. The advantages of the isothermal method include elimination of thermal lag effects and minimizing interferences due to decomposition.[33–35] In particular, the isothermal mode more or less reflects the nature of the direct chemical reaction (gravimetry) as compared to the scanning mode. The calculation of the kinetic parameters of the isothermal mode needs at least three isothermal experiments at different temperatures since the reaction rate coefficient is a function of temperature.

Figure 6 shows the DSC isothermal traces of the formations of cross-linked PDMSU(CPDMSU) and CPMMA using VAZO 52 and BPO as an initiator at 70 °C. The behavior of the cross-linking PDMSU can be classified as a typical "nth" order reaction ($\mathrm{d}a/\mathrm{d}t = -K(T)\,(1 - a)^n$)[35] as shown in curve a. The reaction order n of CPDMSU is 1.6. The rate of the reaction is a maximum at the initial concentration of the components. Curve b indicated that the formation of CPMMA by VAZO 52 behaves as an "autoaccelerating" reaction (due to the Trommsdorff–Norrish effect), and the overall reaction order n was near to first order. The gelation time corresponding to the time when the maximum in heat evolution of the reaction appears for the CPMMA is 10 min. However, if BPO was used as an initiator instead of VAZO 52, the gelation time of CPMMA occurred 30 min later (curve c). This implies that the formation of a PDMSU network has been essentially completed while only a few MMA monomers polymerized. The larger difference between the gelation time is simply due to the larger gap of activation energies

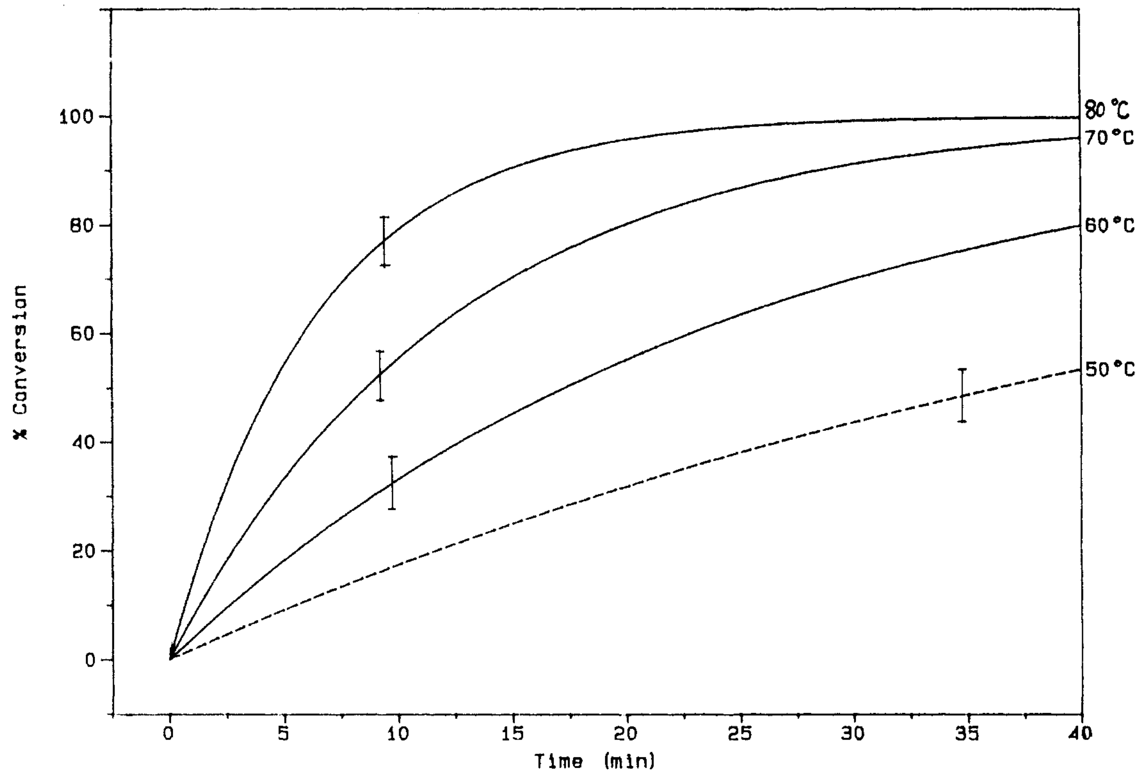


Figure 4. Conversion versus time of the formation of PDMSU/PMMA (50%) IPN based on a scanning rate of 5 °C/min (with VAZO 52 initiator).

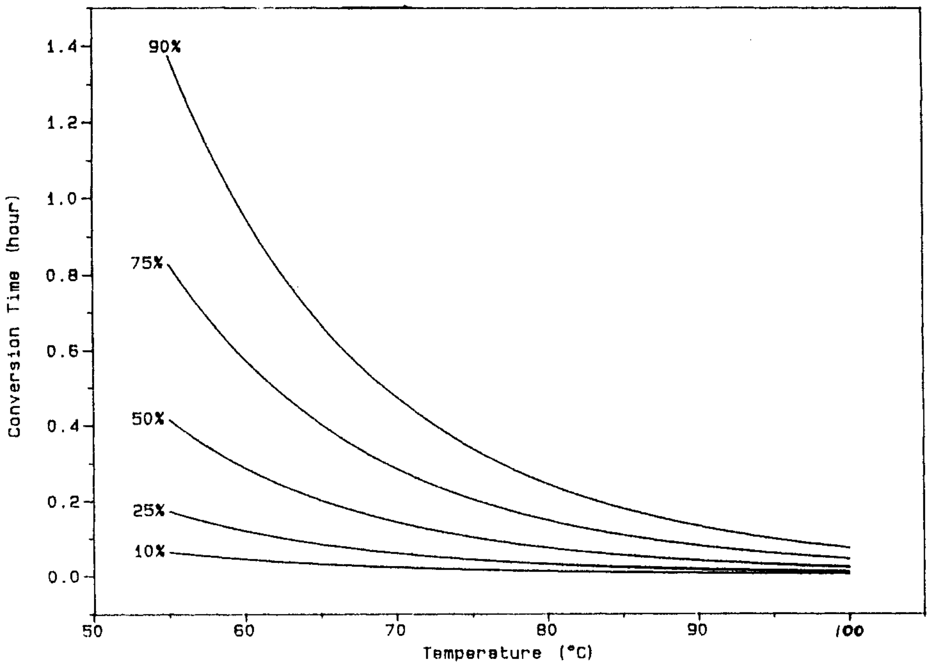


Figure 5. Conversion time versus temperature of the formation of PDMSU/PMMA (50) IPN based on a scanning rate of 5 °C/min.

of decomposition between VAZO and BPO. The conversion of CPDMSU versus time at different temperatures was calculated from the DSC isothermal mode (Figure 7). The curves showed that the conversion of CPDMSU is about 80% at 70 °C after 12 min which is near to the theoretical prediction of the gel point of CPDMSU of 0.816 according to the Flory equation[36]

$$P_G = \{1 + p(f - 2)\}^{-1/2} \qquad (6)$$

with P_G the critical extent of reaction for gelation, p the number of hydroxyl groups on branch units divided by the total number of such groups present, and f is the functionality of the branching unit, which is 3 in our case.

Figure 8 shows the DSC isothermal traces of IPN formation using different initiators. Curve a shows two exothermal peaks, the first one clearly belongs to the cross-linking of PDMSU and the second one is mainly due to the cross-linking polymerization of MMA by BPO. The broad exothermal peak of the MMA reaction is due to the "cage" effect in PDMSU network formation (where polymerization of MMA is subject to diffusion control[11]). However, only one narrow exothermal peak has been observed in curve b which characterizes both cross-linking reactions of PDMSU and PMMA (by VAZO) in this IPN formation with well-matched rates of reactions.

Figure 9 shows the conversion versus time curve of IPN formation in which the dashed line curve comes from the DSC isothermal mode, and the solid line is based on the gravimetric analysis of conversion data. The results for both experiments are in very good agreement within the

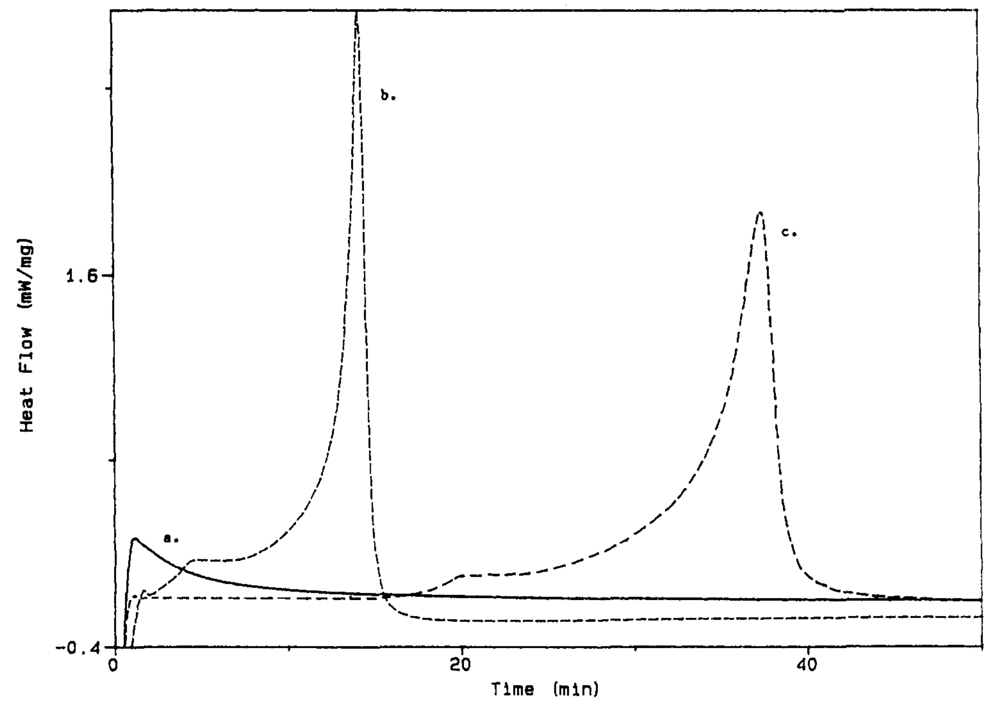


Figure 6. DSC isothermal mode traces of (a) the formation of PDMSU, (b) CPMMA by VAZO 52, and (c) CPMMA by BPO, at 70 °C.

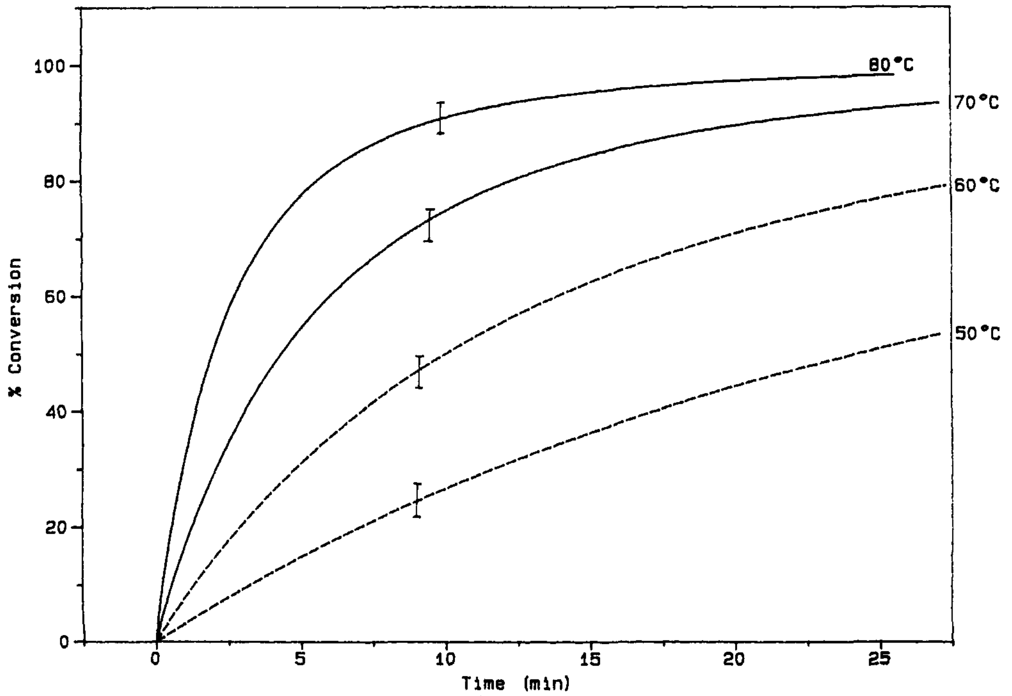


Figure 7. Conversion versus time of the formation of PDMSU based on the DSC isothermal mode.

range of experimental error. However, higher values by about 20% of the conversion to PDMSU/PMMA SIPN are observed from the DSC scanning mode (Figure 5) as compared to those observed in the DSC isothermal mode. Such overestimated values due to the thermal gradient effects and nonlinear heating ramps in the DSC scanning mode have been previously reported.[33-35] On the other hand, some errors in the DSC isothermal mode could be due to some reaction of -NCO with OH groups which occurred before the cell and sample achieved equilibrium temperature, and some cross-linking reactions were not completed yet in the interval given by isothermal mode network formation time and which thus led to some amount of unrecorded heat.

Clearly DSC methods (just like IR) cannot yield the complete mechanism of these reactions in SIPN formation. Since the overall kinetic description of IPN formation requires strictly two different conversions for each of the network species monomers (which requires that the exothermal peaks appearing in the DSC measurement should not overlap). Thus, use of a single, average mass conversion implies a number of simplifying approximations. E.g., it is clearly valid if the rates of conversion of the monomers producing network i ($i = 1, 2$), a_i, are equal and involve simple $\alpha + \beta$ order kinetics in the reactants (this is not unlikely since IPN formation requires the 1-network and 2-network to be entangled) for then we have $da_1/dt = -k(1 - a_1)^{\alpha}(1 - a_2)^{\beta} = da_2/dt$ and thus $a_1 = a_2$, and if X is the weight fraction of the network, $a = Xa_1 + (1 - X)a_2 = a_1$, so that the overall kinetics can be written

$$da/dt = -k_1(1 - a_1)^{\alpha}(1 - a_2)^{\beta}$$

$$da/dt = -k(1 - a)^{\alpha+\beta}$$

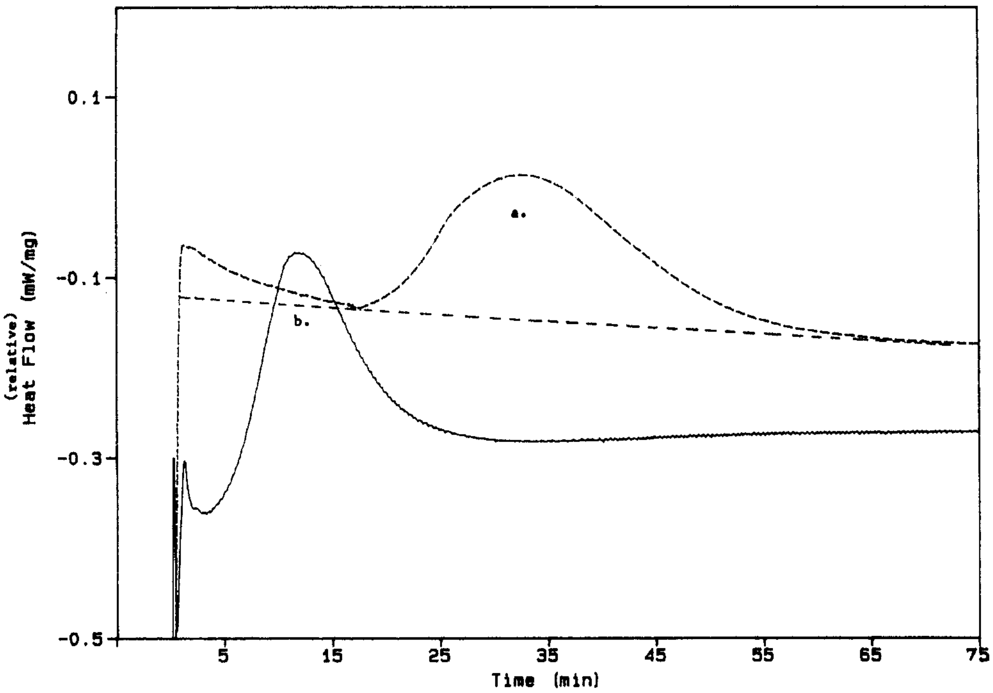


Figure 8. DSC isothermal mode traces of IPNs formation at 70 °C, using (a) BPO and (b) VAZO 52.

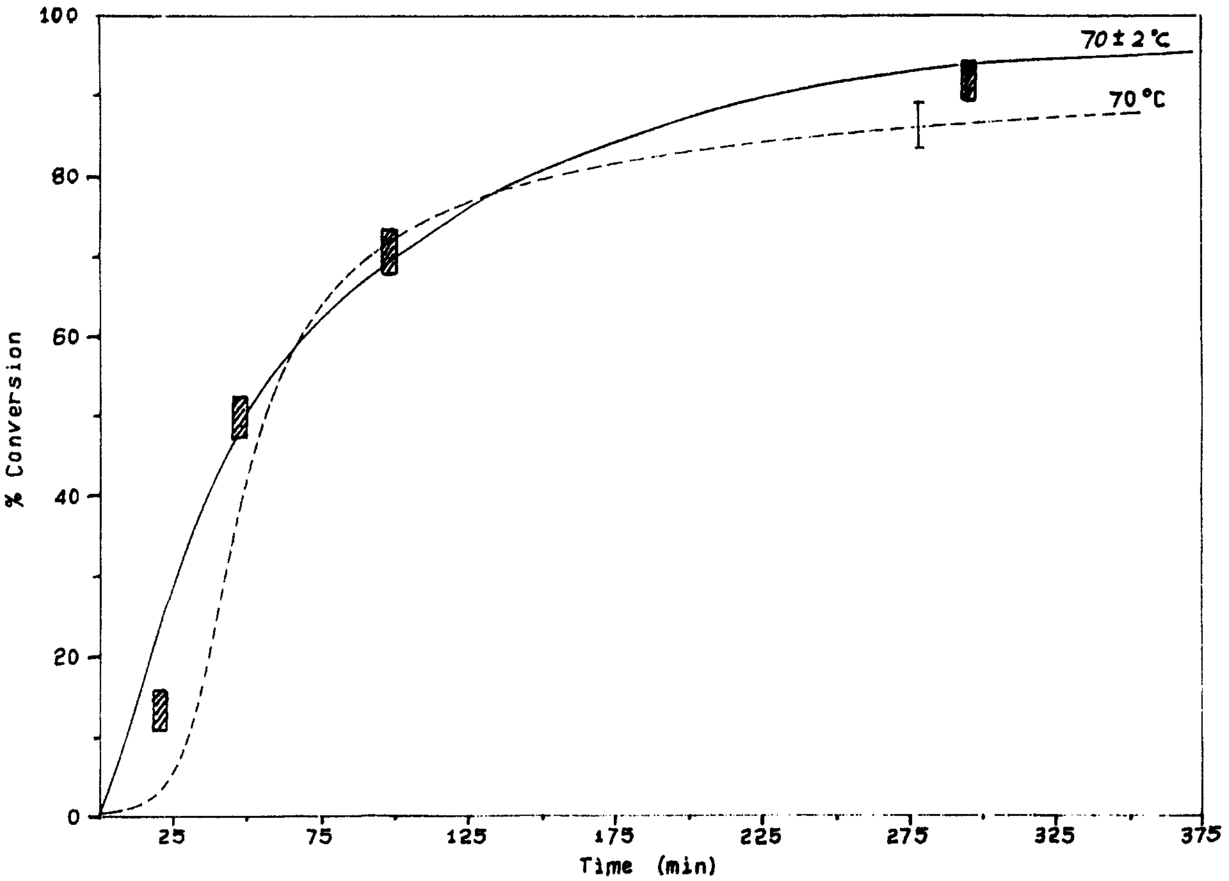


Figure 9. Conversion versus time of the formation of IPN with 50 wt % PDMSU: (a, dashed line) DSC isothermal mode data; (b solid line) gravimetric data.

$$d\alpha/dt = -k(1-\alpha)^n$$

with $n = \alpha + \beta$; of course, if the rates of individual network formation are not roughly equal, this argument fails.

Phase Morphology Studies. The phase morphology studies of the IPNs were carried out immediately following the DSC isothermal mode kinetics studies in which the IPN samples were prepared. T_gs of these samples were obtained by DSC. Figure 10 shows DSC traces of the blend of linear PMMA/PDMSU (curve a), 80 and 50 wt % PDMSU/PMMA IPN using BPO as an initiator (curves b and c). Curve a indicates that the blend of linear PDMSU and PMMA is immiscible with two T_gs. The lower T_g (−111.3 °C) and the higher one (99.6 °C) correspond to that of the pure components PDMSU and PMMA, respectively. The IPNs of PDMSU/PMMA also exhibited phase separation with several T_gs (curves b and c).

Figure 11 shows that the phase morphologies of PDMSU/PMMA (at 80% and 50% PDMSU0 have been

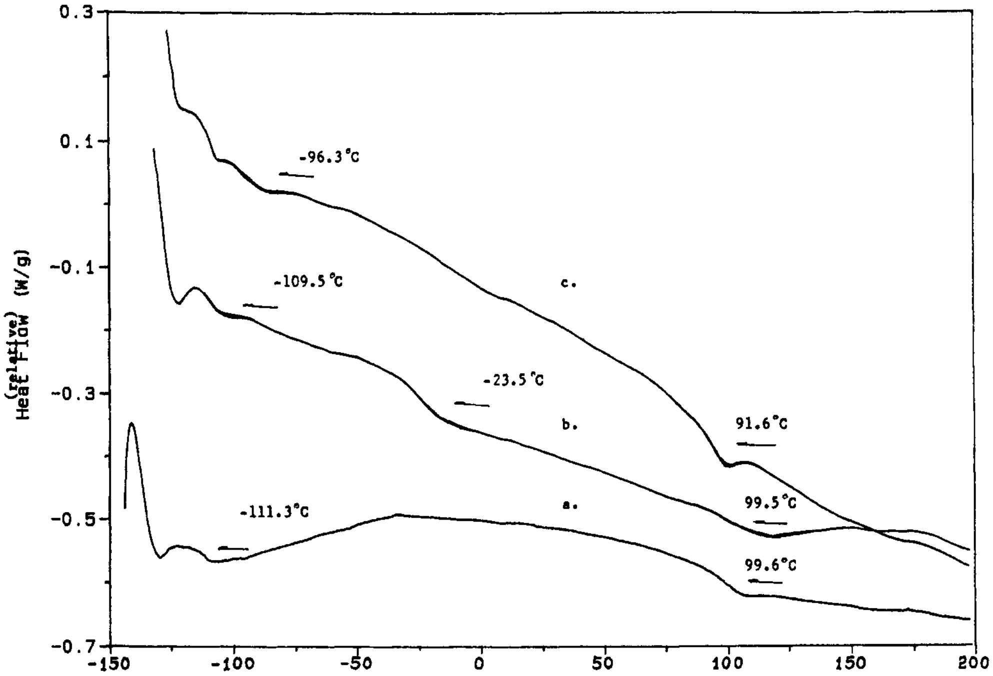


Figure 10. DSC traces of (a) the blend of linear 50 wt % PDMSU and linear PMMA, (b) IPN with 80 wt % PDMSU, with BPO as an initiator, and (c) IPN with 50 wt % PDMSU, with BPO as an initiator.

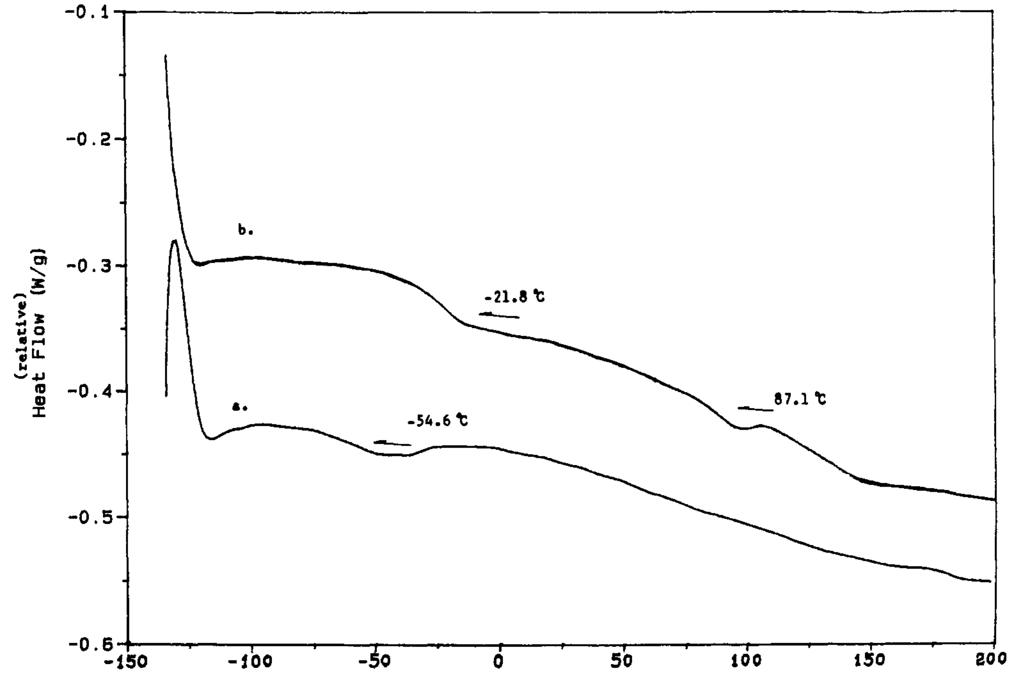
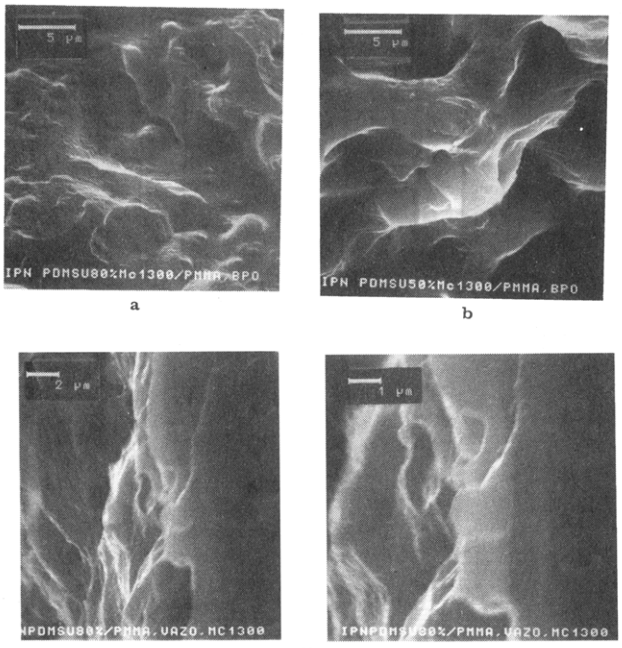


Figure 11. DSC traces of (a) IPN with 80% PDMSU, with VAZO 52 as an initiator, and (b) IPN with 50% PDMSU, with VAZO as an initiator.

changed from these totally immiscible IPNs (cf. Figure 10) into more miscible ones by using VAZO 52 as an initiator instead of BPO. The IPN of 80% PDMSU/PMMA now exhibited a single phase with only one glass transition at -54.6 °C (curve a). Even the IPN with 50% PDMSU became more miscible in the same that the T_gs shifted inward from -111.3 and +96.6 °C of the pure PDMSU and PMMA (curve b). This clearly indicates that the apparent miscibility of simultaneous IPN can be improved by changing the rates of the cross-linking reactions employed in the IPN formation.

DSC measurements of the IPNs of PDMSU/PMMA were further confirmed by SEM obervation. Samples which were made for gravimetric studies employed the same reaction conditions (e.g., temperature) as those used in the DSC isothermal mode studies were used for SEM investigations. The SEM micrographs of the IPNs of PDMSU/PMMA (using BPO) (80% and 50% PDMSU) clearly showed a heterogeneous surface (Figure 12a,b). The SEM phase domain size of the IPN with 80% PDMSU had reached a mean diameter of 0.8 μm or more. PMMA formed the discontinuous phase. At higher PMMA content the binary phase morphology (with multiple layers) of the IPN with 50% PDMSU (using BPO as initiator) can be seen from Figure 12b, where the thickness of the layer is about 0.2 μm. However, the IPN of 80% PDMSU/PMMA (using VAZO as initiator) now presents a homogeneous surface under SEM observation even when the magnification was increased from 5000 to 10 000 (Figure 12c,d). Thus the SEM observation confirmed the DSC



a b c d

Figure 12. SEM micrographs of the IPNs of (a) 80% PDMSU/PMMA (BPO initiator), (b) 50% PDMSU/PMMA (BPO initiator), and (c) 80% PDMSU/PMMA (VAZO 52 initiator), ×5000 and (d) ×10 000. In the upper two micrographs the phase separation is evident in the separated layers and domains which are absent in the lower two micrographs.

results. The sample with one T_g has no observable SEM phase domain; the samples with two T_gs have heterogeneous SEM phase morphologies.

Conclusion

Kinetics of simultaneous IPN of PDMSU/PMMA have been carried out by DSC by means of computer-aided DSC data analysis programs. The kinetic parameters of the SIPN formation such as conversion versus time and temperature, heat of reaction, activation energy, and reaction order have been studied via DSC scanning and isothermal modes. The results from the DSC experiment are in good agreement with those obtained from the gravimetric experiment. The experimental evidence clearly showed that the phase morphologies of SIPNs of PDMSU/PMMA can be changed by changing the rates of the cross-linking reactions. An apparently miscible IPN of 80% PDMSU/PMMA can be made if the gelation times for both networks match. This sample possessed one T_g and had no observable SEM phase domains. The phase-separated IPN with the same composition of PDMSU was prepared by choosing rather different gelation times for the two cross-linking reactions. This sample showed two T_gs and a heterogeneous phase morphology under SEM observation.

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