Isothermal Reaction Kinetics and Phase Behavior Analysis in the Formation of PCU/PMMA Interpenetrating Polymer Networks

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ABSTRACT: Isothermal reaction kinetic and phase behavior studies have been carried out on simultaneous interpenetrating polymer networks (SIPNs) of poly(carbonate-urethane) (PCU)/poly(methyl methacrylate) (PMMA) and related materials via differential scanning calorimetry (DSC) with a computer-aided DSC data analysis program. The kinetic parameters such as conversion versus time and temperature, activation energy, and reaction order have been investigated by a DSC isothermal method. The data from the DSC isothermal experiment are in good agreement with gravimetric kinetic data. The phase behavior of SIPNs of PCU/PMMA and related materials have been analyzed by means of DSC, SEM, and TEM. The results showed that the original one phase morphology of SIPNs of PCU/PMMA can be changed to a two phase morphopogy by changing the kinetics of network formation. Two phase SIPN of PCU/PMMA have been obtained by employing nonsimultaneous cross-linking reactions for the two different networks while a one phase SIPN of PCU/PMMA can be made if the gelation times for both networks matched. The T_g's of the products increased with the increasing degree of conversion, possibly due to higher degrees of cross-linking with higher conversion.

Introduction

In a previous paper[1] the kinetic studies of simultaneous interpenetrating polymer networks (SIPN) of poly(dimethylsiloxane-urethane) (PDMSU)/poly(methyl methacrylate) (PMMA) have been investigated by means of differential scanning calorimetry (DSC) with a computer-aided DSC data analysis program. The experimental evidence clearly showed that the miscibility of SIPNs of PDMSU/PMMA can be greatly improved by changing the rates of the cross-linking reactions. A miscible IPN of 80 wt % PDMSU/PMMA has been made when the gelation times for both networks match even though SIPNs of 80 wt % PDMSU/PMMA were originally prepared as multiple phase materials.[2] When the rate of cross-linking did not match well, phase separation was expected due to the large differences in solubility parameters (δ) and glass transition temperatures (T_g's of their linear components[3] (the calculated solubility parameters of linear PMMA $\delta = 9.2$ (cal/cm^3), PDMSU $\delta = 8.0$ (cal/cm^3); T_g(PMMA) = 100 °C, T_g(PDMSU) = −110 °C.[4]

This raised the question if the phase morphology of a SIPN which was originally prepared as a one phase material could be changed to a two phase material by producing a mismatch of the gelation times of the two networks. Fully miscible SIPNs, poly(carbonate-urethane) (PCU)/poly(methyl methacrylate) (PMMA), have been prepared and characterized by us.[5] As we suggested, their one phase behavior may roughly correlate with the smaller difference in solubility parameter and T_g's of their linear components,[3] (the calculated solubility parametrs of linear PCU $\delta = 8.8$ (cal/cm^3), PMMA $\delta = 9.2$ (cal/cm^3), T_g(PCU) = −30 °C, T_g(PMMA) = 100 °C).[4] The forced mixing by near simultaneous gelations may also be caused by kinetic effects. In the original preparation of the one phase SIPN of PCU/PMMA,[5] the PCU was a hydroxyl-terminated poly(hexamethylene carbonate) cross-linked with biuret triisocyanate (BTI) obtained from hexamethylene diisocyanate (HDI). The cross-linked PMMA was prepared by benzoyl peroxide (BPO) or redox initiator *N,N*-dimethylaniline (DMA)/BPO and used ethylene glycol dimethacrylate (EGDMA) as a cross-linker. Over the full composition range (30-90 wt % of PCU), the SIPNs of PCU/PMMA were transparent, essentially colorless solids with a single T_g, and no TEM resolvable phase domains.

In the next section a direct experiment has been designed to change the kinetics of SIPN PCU/PMMA. DSC is used to monitor the entire course of the cross-linking reactions. It was found that with the slower cross-linking reaction rate of PMMA in PCU/PMMA SIPN formation obtained by using as initiator dicumyl peroxide (DCP) instead of DMA/BPO or BPO causes the IPN to phase separate. We also prepared the sequential IPN of PCU/PMMA which was phase separated.

Experimental Section

1. **Materials.** The raw materials used and their designations are listed in Table 1. Methyl methacrylate (MMA), HDI, and EGDMA were distilled in a stream of nitrogen under vacuum and were stored over 4-Å molecular sieves in a refrigerator. The linear hydroxyl-terminated polycarbonates (PC) were dissolved in toluene, then precipitated in petroleum ether, and dried at 50 °C in a vacuum for 24 h. BPO and DCP were dried at room temperature under vacuum for 2 days. The aliphatic polyisocyanate based on 1,6-hexamethylene diisocyanate, biuret triisocyanate (BTI) (Desmodur n-100), *N,N*-dimethylaniline (DMA), and HDI were used without further purification. The isocyanate functionality of the BTI was found to be 2.62 by the *n*-dibutylamine (DBA) titration method.[6]

The synthesis of the SIPNs, pseudo-IPNs, and blends of the linear components as well as the pure cross-linked networks of PCU and PMMA are same as those described in ref 5 except that some of the SIPNs were prepared using DCP as an initiator and without the solvent toluene.

The sequential IPN of PCU/PMMA was prepared by swelling the PCU network with a solution of MMA containing the cross-linker EGDMA and the initiator BPO in a refrigerator (at about 5 °C) until the PCU took up about 25 wt % of the MMA solution. This was transferred to another container and sealed under a N_2 atmosphere. The sample was then put in an oven at 70 °C for 3 days to polymerize the MMA completely. The product was precipitated in methanol, vacuum dried at 80 °C for 48 h, and then weighed. The composition of the sequential IPN of PCU and PMMA was about 80 wt % of the PCU. The product is an almost colorless, transparent solid. The molecular weight

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Table 1. Raw Materials Employed and Their Abbreviation

designation	name and description	source
PC (Duracarb 120 series)	poly(1,6-hexanediol–carbonate)s, MW 850, 2000; hydroxyl functionality 2.0	PPG Industries
BTI (Desmodur N-100)	Biuret triisocyanate derived from hexamethylene diisocyanate; isocyanate functionality 2.62	Mobay Chemical Co.
MMA	methyl methacrylate	Aldrich Chemical Co.
EGDMA	ethylene glycol dimethacrylate	Aldrich Chemical Co.
BPO	benzoyl peroxide (97%)	Aldrich Chemical Co.
DCP	dicumyl peroxide	Aldrich Chemical Co.
DMA	*N,N*-dimethylaniline (99%)	Aldrich Chemical Co.
DBA	*n*-dibutylamine (99%)	Aldrich Chemical Co.
HDI	hexamethylene diisocyanate (98%)	Aldrich Chemical Co.
VAZO 52	2,2′-azobis(2,4-dimethylvaleronitrile)	DuPont Co.
methanol	solvent grade	Aldrich Chemical Co.

between cross-links ($\bar{M}_c$) of the PCU and PMMA is 1000 and 4000 separately from the employed raw material stoichiometry.

The conversion of IPNs, pseudo-IPNs, and blends could also be determined gravimetrically as a function of time. Aliquots of the IPN polymerization mixture were terminated at various time intervals by pouring them into a solution of methanol with 0.1 wt % hydroquinone which was then vigorously stirred for 4 h and precipitated overnight. The product was then washed several times with fresh methanol. The products were dried under vacuum at 80 °C for 48 h and weighed. The conversion of the monomers was calculated from this weight.

2. Instrumental Methods and Procedures. Isothermal reaction kinetics of the formation of the PCU/PMMA IPN have been carried out on a DSC (2910 TA Instruments) with a computer-aided data analysis software program. In the DSC isothermal method the reaction exothermic rate versus time was recorded. The isothermal method offers the advantages of greater simplicity of data interpretation and broader applicability. Generally, the isothermal method often provides more reliable kinetic information because it eliminates thermal lag effects and minimizes decomposition interference.[7-10]

In the DSC isothermal mode method if the reaction obeys

$$\mathrm{d}a/\mathrm{d}t = -K(T)(1-a)^n \qquad (1)$$

with da/dt the reaction rate (1/s), a the fractional conversion after time t, $K(T)$ the specific rate constant at temperature T, and n the reaction order, for an nth order reaction, the rate constant and the reaction order can be obtained from the intercept and the slope of a log(da/dt) versus log $(1 - a)$ plot. The two basic parameters (da/dt and a) required for the analyses are obtained from the DSC exotherm. The reaction rate is determined by dividing the peak height, dH/dt, at time t by the total heat of the reaction, ΔH_0.

$$\mathrm{d}a/\mathrm{d}t = (\mathrm{d}H/\mathrm{d}t)/\Delta H_0 \qquad (2)$$

The value of a can be obtained by measuring the partial heat of reaction up to time t, ΔH_p, and dividing by the total heat of the reaction.

$$a = \Delta H_p/\Delta H_0 \qquad (3)$$

The calculation of the kinetic parameters of the isothermal reaction requires at least three isothermal experiments at different temperatures since the reaction rate coefficient is a function of temperature. The details of the procedure and operation are described in ref 1, and the baseline and cell constant of the DSC were calculated in accord with the DSC kinetic data analysis program before commencing the DSC kinetic studies.

3. Characterization. Soxhlet extractions of the IPNs of PCU/PMMA were carried out by using toluene as solvent for a period of 48 h.

The phase morphology of the IPNs was studied by means of DSC, SEM, and TEM. The samples from the DSC isothermal reaction were used to test their T_g's. DSC measurements were carried out between −100 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 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 in the gravimetric experiments at the same concentrations and temperatures as employed in the DSC isothermal mode experiments.

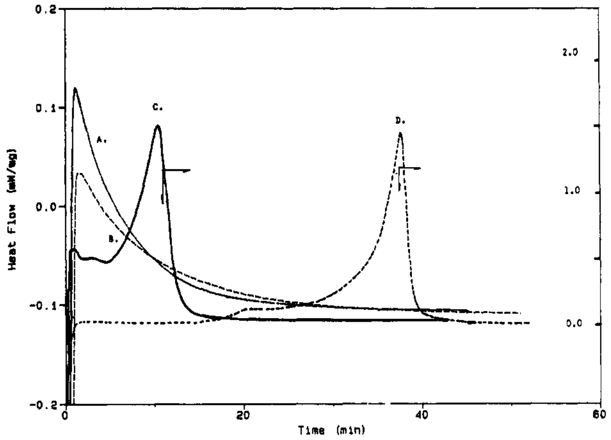

Figure 1. DSC traces of the formation of (A) PCU at 80 °C, (B) PCU at 70 °C, (C) C-PMMA using the redox initiator BPO/DMA, and (D) C-PMMA using the initiator BPO.

TEM micrographs were taken on a Philips 300 transmission electron microscope. The preparation of the specimens for electron microscopy was as follows: All samples were slivered and the shavings stained for 3 days in 4% aqueous osmium tetroxide. They were then rinsed briefly and dried, after which they were embedded in Spurr resin. Sections were cut with glass knives on an LKB Ultratome III, were subsequently stained with uranyl acetate and lead citrate, and were then viewed.

SEM micrographs were taken on a digital scanning microscope (DSM 940, Zeiss, Germany). The specimens were frozen under liquid nitrogen and 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 000X.

Results and Discussion

1. Isothermal Reaction Behavior. Figure 1 shows the DSC isothermal reaction curves for PCU and PMMA formation. Clearly, the formation of PCU behaves as an nth order reaction. The rate of the reaction of PCU exhibited a maximum in the initial concentration of the reactants; the rate of the reaction was also increased with increasing temperature (curves a and b). The reaction order n is 1.2 ± 0.08, and the activation energy is 34 ± 0.4 kJ/mol. Similar results have been reported for the polyurethane system when they were measured by FT-IR.[11,12] Curves c and d represent the formation of CPMMA using DMA/BPO and BPO as initiators, respectively which indicated a typical "autoaccelerating" reaction behavior (Trommsdoff effect). The investigation of the kinetics of PMMA formation was reported in ref 1.

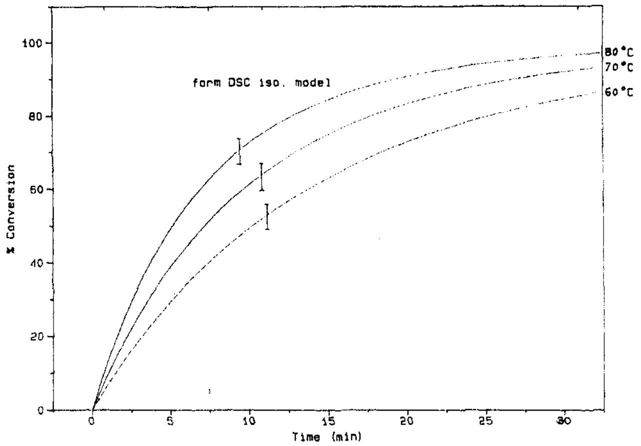

Figure 2. Conversion versus time of the formation of PCU from the DSC isothermal mode reaction at different temperatures.

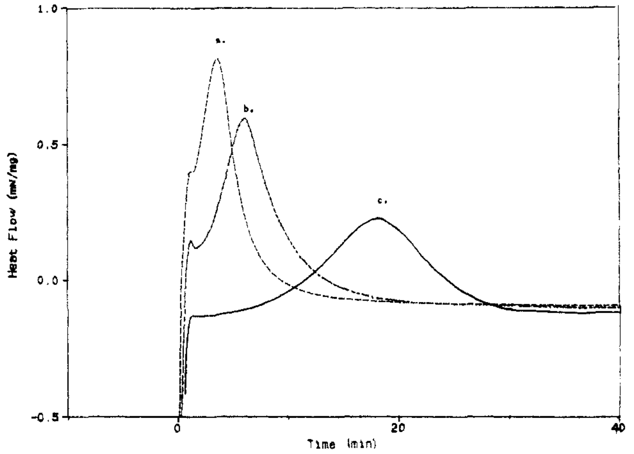

Figure 3. DSC traces of the IPN formation of 50 wt % PCU/PMMA (a) using DMA/BPO at 70 °C and (b) at 60 °C and (c) using the initiator BPO at 70 °C.

The conversion versus time of PCU formation obtained from the DSC isothermal experiment is shown in Figure 2. The conversion of PCU reached about 70 wt % after 12 min, which was quite near the theoretical gel point (0.786) predicted from the Flory statistical theory.[13]

$$P_G = 1/(f-1)^{1/2} \tag{4}$$

with P_G the critical extent of reaction for gelation and f the functionality of the isocyanate groups in BTI, which is 2.62 in our case. At this point (12 min) in the isothermal reaction curve, the gelation of CPMMA occurred, which corresponded to the maximum in heat evolution. This means that the gelations of PCU and PMMA are very close in the DSC isothermal experiment. The gel point of the cross-linking polymerization of MMA monomer associated with the viscosity of the polymerizating mixture suddenly goes up and loses fluidity meanwhile it releases a large amount of heat of reaction. This has been observed directly.[14] The experimentally observed gelation ranges of the cross-linking polymerization of MMA by BPO and redox initiator BPO/DMA are about 32 ± 2 and 11 ± 1 min at 70 ± 2 °C, respectively, which are close to the times when the maxima in heat evolution appeared in the DSC isothermal reaction curves.

Figure 3 represents the DSC isothermal reaction curves of the IPNs of PCU/PMMA (50 wt %) using BPO as initiator or the redox initiator DMA/BPO at 70 °C. Apparently, only one exothermal peak is produced in the IPN formation, which indicated that both cross-linking reactions proceeded with well matched rates, especially for the IPN using the redox initiator DMA/BPO, even at the lower reaction temperature (curves a and b). The formation of the IPN using BPO showed only one (but broader) exothermal peak (it was noted that a maximum in heat evolution (18 min) appeared much earlier than that found in the formation of the PDMSU/PMMA IPN (35 min).[1]). This earlier onset of the Trommsdoff effect in the formation of PCU/PMMA might reflect the effect of the higher viscosity of the cross-linker BTI.

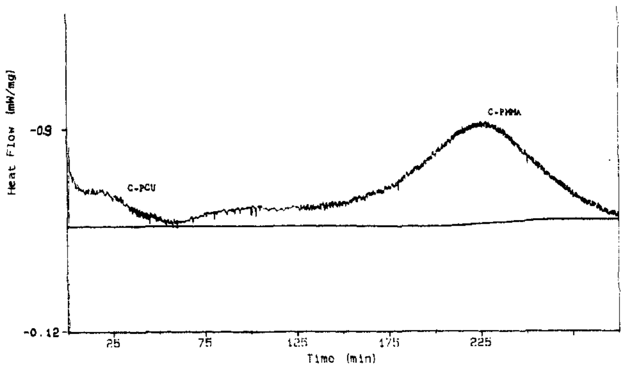

Figure 4. DSC traces of IPN formation of 50 wt % PCU/PMMA using the initiator DCP at 74.3 °C.

Figure 4 shows the DSC isothermal reaction curve of the formation of the 50 wt % PCU/PMMA IPN using DCP as an initiator at 74.3 °C. Two exothermal peaks in the formation of the IPN were observed. The first one clearly belongs to the cross-linking reaction of PCU. After the PCU network formation was completed, a second peak of heat evolution occurs at 225 min due to the cross-linking polymerization of the MMA monomer. The smaller rate of the reaction in the CPMMA formation is due to the smaller decomposition constant (K_d) of DCP ($K_{d\ \mathrm{DCP}}$ = 2.05×10^{-5} at 115 °C, $K_{d\ \mathrm{BPO}} = 4.8 \times 10^{-5}$ at 80 °C).[15] This situation is somewhat similar to the preparation of the sequential IPN in which one network was first made and then the next one was formed.

It is noted that the DSC isothermal reaction behavior of the PCU/PMMA IPN formation changed with different compositions. A very broad exothermal peak (from 5 to 25 min) of the reaction was observed in the formation of 75 wt % PCU/PMMA IPN because of the large "cage" effect in the PCU network formation in which the cross-linking reaction of MMA is subject to slow diffusion control. With increasing MMA concentration, the exothermal peak of the reactions becomes sharper and occurs later (from 25 to 38 min), which might be due to the "solvent" effect of the MMA monomers.[16,17] This produces possibly nonsimultaneous gelations of the two cross-linking networks. The IPNs of PCU/PS (polystyrene) and PCU/PVP (poly(vinylpyridine)) with a PCU content above 50 wt % exhibited one phase morphologies but two phases for the IPNs with 50 wt % or below PCU content.[18,19] The phase morphology of the IPN of PCU/PMMA with 25 wt % PCU content was changed from one phase into two phases 1.5 years after its preparation; on the other hand, IPNs with higher PCU contents (50 wt % and above) still maintained one phase morphologies after 1.5 years[20] had passed since their synthesis. We speculate that this might be related to the nonsimultaneous gelations of the two cross-linking networks in these IPNs with higher content of substituted vinyl monomers.

The isothermal reaction behavior for the formation of the IPNs of PCU/PMMA with different $\bar{M}_c$'s of PCU showed that the higher the molecular weight of the polycarbonate diol (PC) oligomer used, the sooner the Trommsdoff effect appeared (the maximum heats of

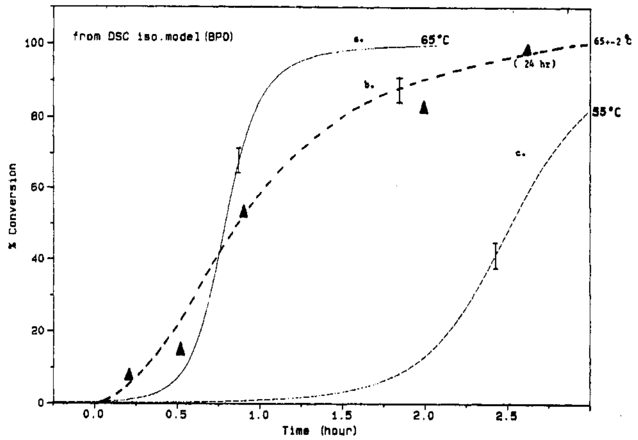

Figure 5. Conversion versus time of the formation of the 50 wt % PMMA/PCU IPN at different temperatures: (a) and (c) from the DSC isothermal mode reaction; (b) from the gravimetric experiment.

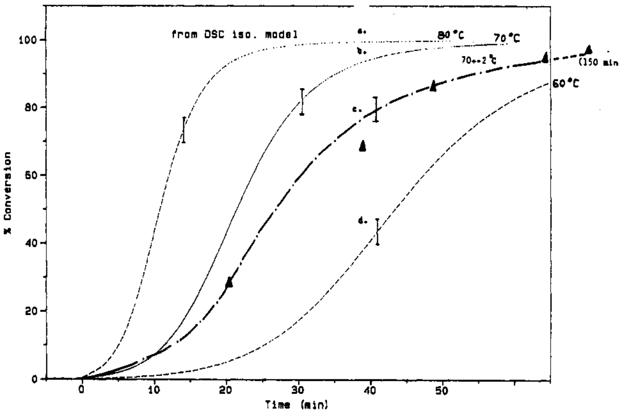

Figure 6. Conversion versus time of the formation of the 50 wt % C-PMMA/L-PCU pseudo-IPN at different temperatures: (a), (b), and (d) from the DSC isothermal mode reaction; (c) from the gravimetric experiment.

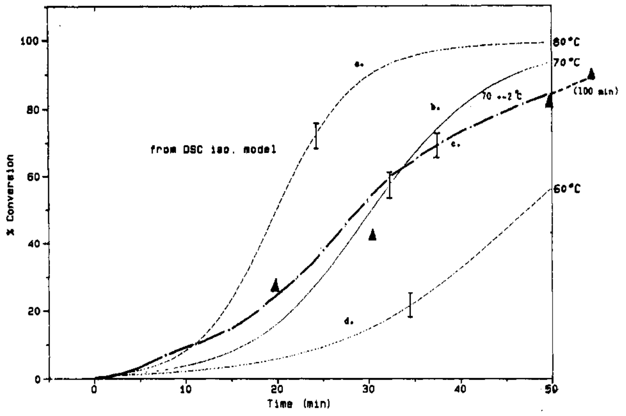

Figure 7. Conversion versus time of the formation of the 50 wt % L-PMMA/C-PCU pseudo-IPN at different temperatures: (a), (b), and (d) from the DSC isothermal mode reaction; (c) from the gravimetric experiment.

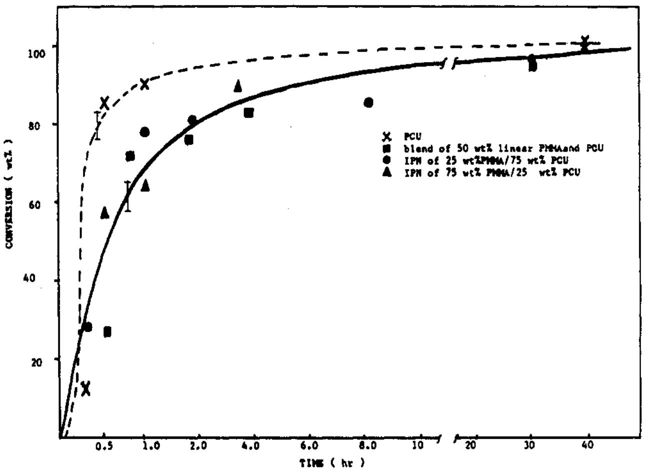

Figure 8. Conversion versus time of the formation of pure PCU, the blend of linear polymers, and IPNs of PCU/PMMA at 70 °C.

reaction occur in 12 and 18 min for $\bar{M}_c$'s of PCU of 2200 and 1100, respectively). This is mainly due to the effect of the high viscosity of the high MW PC oligomer used. On the other hand, the earliest Trommsdoff effect (13 min) was observed in the pseudo-IPN with cross-linked PMMA (C-PMMA) and linear PCU (L-PCU) components. The Trommsdoff effect was postponed (32 min) in the formation of the blend of L-PMMA and L-PCU because of the higher molecular mobility of the components in these non-cross-linking reactions.

2. Comparison of DSC Isothermal Reaction and Gravimetric Experiment Conversions. The conversion versus time curves of the formation of PCU/PMMA IPNs and related materials (pseudo-IPNs, etc.) were obtained from the DSC isothermal mode reaction via a computer-aided data analysis program. Gravimetric conversion data at the same concentrations and temperatures were obtained to compare with DSC isothermal mode conversions. Figure 5 shows that the conversions of the 50 wt % PCU/PMMA IPN from the gravimetric experiment agree well with the early stage of the conversion (about 1 h) data from the DSC isothermal mode experiment. However, the rates of the reactions in the gravimetric experiment became smaller in the later stage of the reactions compared to those of the DSC isothermal experiment. This is also observed in the formation of the pseudo-IPN in which PMMA was cross-linked and PCU was linear (Figure 6). Possibly, this is due to the difficulty of controlling the reaction temperature in the later stages of the bulk reaction in the gravimetric experiment, the mobility of the MMA monomer is limited because of the high viscosity of the system. Figure 7 gives further support for this explanation. The data from the gravimetric experiment for the formation of the pseudo-IPN of L-PMMA/C-PCU at the same composition and reaction temperature as for the DSC isothermal mode experiment were completely mutually consistent. Here the mobility of the MMA monomer was less limited since no cross-linking occurred.

Figure 8 shows the conversion curves versus time for the formation of PCU/PMMA IPNs, the blend of L-PCU and L-PMMA, and pure cross-linked PCU at 70 ± 2 °C. The conversions of these products were obtained from the gravimetric experiment. Similar polymerization behavior has been observed for blends of 50 wt % L-PCU and L-PMMA and 25 and 75 wt % PMMA/PCU IPNs. If in the earlier stage of the formation of these materials (around the gelation range) a higher initial concentration of PC was used, a higher conversion was obtained in the earlier stage of these reactions, because of the initially higher conversion of PCU in the step polycondensation reaction. This is clearly indicated in the conversion curve versus time of PCU formation (Figure 8), which was in good agreement with the data from the DSC isothermal mode reaction (Figure 2).

3. Phase Behavior Studies. Phase morphology studies of the samples from the gravimetric experiment more or less reflected the nature of the isothermal mode reaction kinetic behavior in the formation of the IPNs and related materials. Figure 9 shows the DSC scanning curves of the pseudo-IPN of 50 wt % C-PCU/L-PMMA from the gravimetric experiment at different conversions. Curve a was obtained from the sample at a pregel point

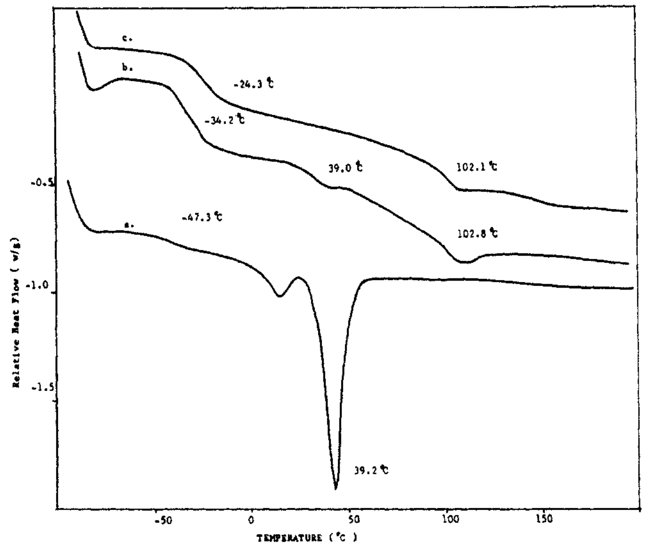

Figure 9. DSC scanning traces of a pseudo-IPN of 50 wt % L-PMMA/C-PCU at different conversions: (a) 30 wt % conversion; (b) 90 wt % conversion; (c) 99.5 wt % conversion.

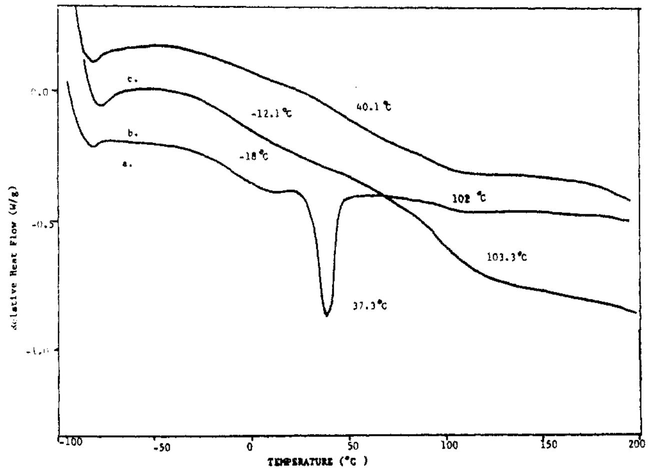

Figure 10. DSC scanning traces of an IPN of 75 wt % PMMA/PCU at different conversions: (a) 26 wt % conversion; (b) 90 wt % conversion; (c) 100 wt % conversion.

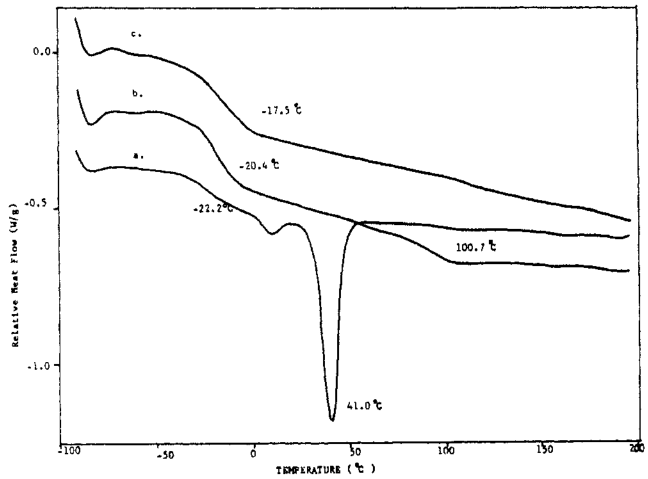

Figure 11. DSC scanning traces of an IPN of 25 wt % PMMA/PCU at different conversions: (a) 60 wt % conversion; (b) 89 wt % conversion; (c) 99 wt % conversion.

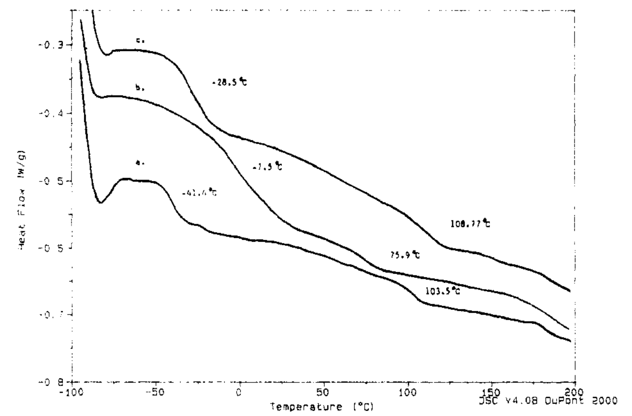

Figure 12. DSC scanning traces of the IPNs and the blend of L-PCU/L-PMMA: (a) blend of 50 wt % L-PCU and 50 wt % L-PMMA; (b) sequential IPN of 80 wt % PCU; (c) IPN of 50 wt % PCU, using the initiator DCP; (d) IPNs of 50 wt % PCU/PMMA using the redox initiator DMA/BPO.

(about 30 wt % conversion) in which the only strong melting endothermal transition (T_m at 39.2 °C) and glass transition temperature (T_g at −47 °C) of the linear PCU have been observed. This indicated that the main reaction was the chain extension reaction of PC at this stage. After the gel point (90 wt % conversion), the melting transition of the linear PCU was greatly decreased and the T_g of the PMMA became predominant. The T_g value of PCU increased continuously with the decreasing extent of the melting transition of linear PCU. Finally, the T_g of PCU reached a maximum at −24.3 °C with the disappearance of the T_m of linear PCU at 100 wt % conversion (curve c). If a small amount of linear PCU was present, it would decrease the T_g of PCU in the system because of the "plasticizing" effect of linear PCU. The T_g's increased with the increasing cross-linking density of the network. A similar phenomenon has been reported in epoxy resin curing.[21,22]

The same behavior was observed for the formation of the IPN of PCU/PMMA. Figure 10 shows the DSC scanning curve of 25 wt % PCU/75 wt % PMMA formation in which the T_g's of PCU increased with the increasing degree of conversion. The sample possesses two T_g's (−12.1 and +102 °C) at 90 wt % conversion; however, only one broad glass transition (at 40.1 °C) was found for the sample at 100 wt % conversion. Similar results have been obtained for the IPN of 75 wt % PCU/25 wt % PMMA (Figure 11). A sample at 89 wt % conversion showed two T_g's (−20.4 and 100.7 °C) but only one T_g at −17.5 °C at 99 wt % conversion. This shows that even a small amount of the linear components present in the IPN of PCU/PMMA would produce multiple T_g's. A one phase IPN of PCU/PMMA can be obtained only at very high conversions and in the absence of the linear components. Soxhlet extraction of the IPNs confirmed that the degree of cross-linking of the IPN increased with the increasing degree of conversion of the IPN. No weight loss of the IPN at 99 wt % conversion was observed after extraction; however, the weight loss of the sample at 89 wt % conversion was about 9.6 wt %, and the sample at 60 wt % conversion (at the pregel point) dissolved almost completely (weight loss 97 wt %) after extraction.

Figure 12 shows the DSC scanning curves of the blend, sequential IPN, and IPNs of PCU/PMMA using different initiators. All of these samples were made in the DSC isothermal reaction mode, except for the sequential IPN. T_g measurements (DSC) of the samples were then immediately carried out after the isothermal reaction in the DSC. Two T_g's are clearly present in curves a–c corresponding to the blend of 50 wt % L-PCU and L-PMMA, the sequential IPN with 80 wt % PCU content, and the full IPN of 50 wt % PCU/PMMA using DCP as an initiator. The lower T_g was near the T_g of pure PCU and the higher T_g reflects that of the PMMA network. However, when the rate of the cross-linking reaction of PMMA was

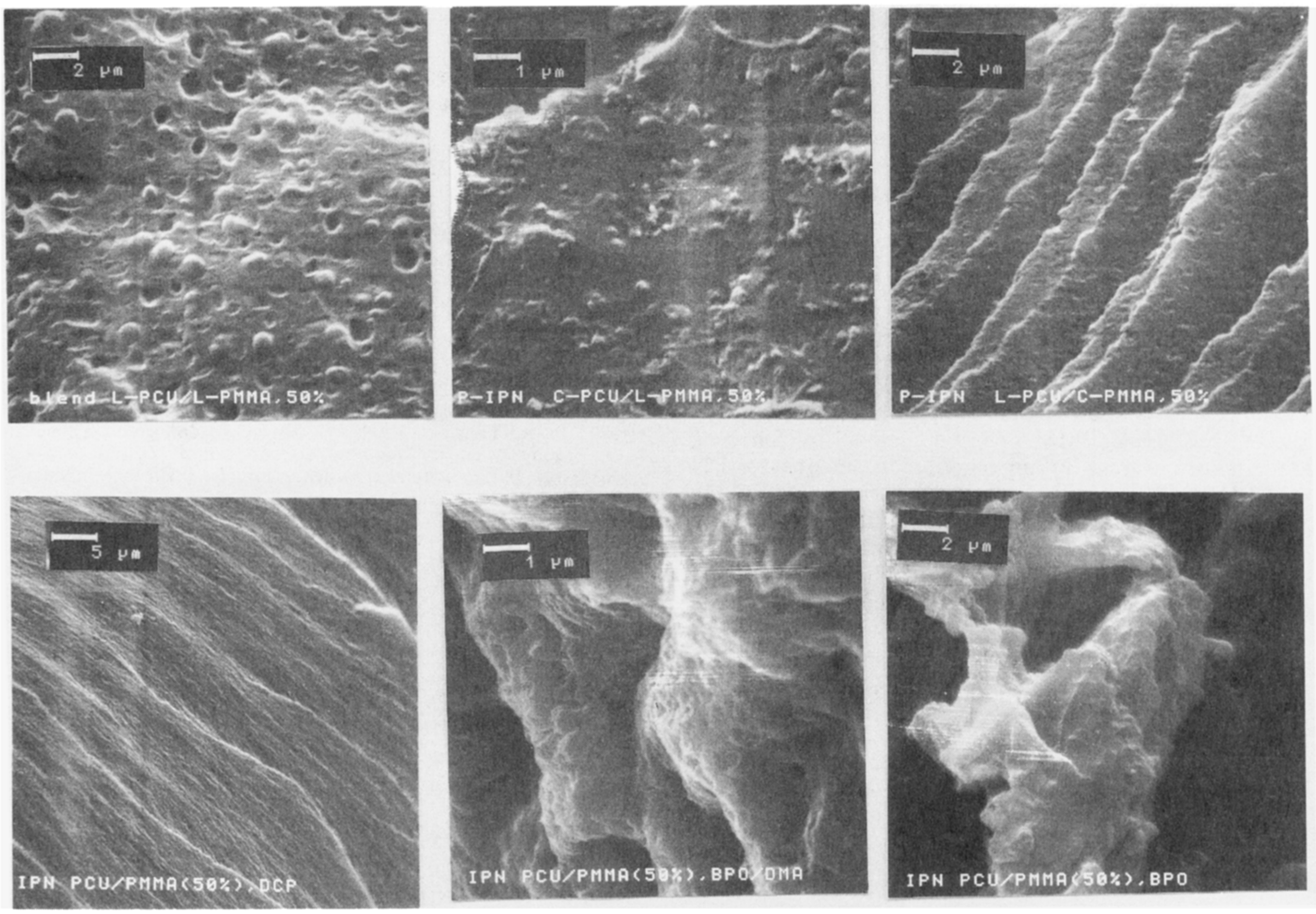

Figure 13. SEM micrographs of (a, top left) a blend of 50 wt % L-PMMA/L-PCU, (b, top middle) a pseudo-IPN of 50 wt % L-PMMA/C-PCU, (c, top right) a pseudo-IPN of 50 wt % C-PMMA/L-PCU, (d, bottom left) an IPN of 50 wt % PMMA/PCU, using initiator DCP, (e, bottom middle) an IPN of 50 wt % PMMA/PCU, using BPO/DMA, and (f, bottom right) an IPN of 50 wt % PMMA/PCU, using BPO.

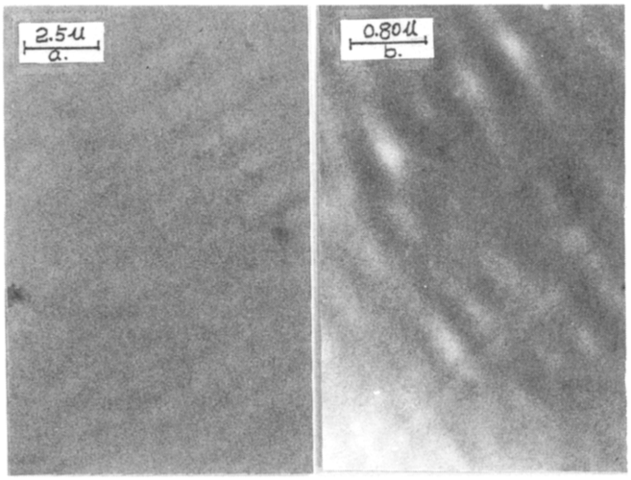

Figure 14. TEM micrographs of the full IPN of 50 wt % PMMA/PCU: (a) ×4485; (b) ×13800.

changed by using the redox initiator DMA/BPO instead of DCP (which made the gelation of the two cross-linking networks occur almost simultaneously), the IPNs of 50 wt % PCU/PMMA exhibited a one phase morphology with only one T_g (curved). This clearly shows that the phase morphology of PCU/PMMA SIPN formation can be changed by changing the rates of the cross-linking reactions of PCU and PMMA.

SEM and TEM observations of these samples confirmed the DSC measurements (Figures 13 and 14). The samples made in the gravimetric experiments had conversions of more than 98 wt %. The SEM micrograph (Figure 13a) of the blend of 50 wt % linear PCU and PMMA exhibited a ball-like multiple phase morphology in which PCU formed the continuous phase. The average PMMA domain size is about 0.8 μm. The smaller PMMA phase domains (mean linear dimension of about 0.2 μm) were distributed in the PCU continuous phase in the pseudo-IPN of C-PCU/L-PMMA, as seen in Figure 13b. On the other hand, the binary phase morphology structure of the pseudo-IPN of 50 wt % L-PCU/C-PMMA is clearly indicated in Figure 13c and had a layer thickness of about 0.4 μm. The IPN of 50 wt % PCU/PMMA using DCP as an initiator showed the same binary phase morphology as that of the pseudo-IPN of L-PCU/C-PMMA and had a layer thickness of about 0.3 μm. (Figure 13d). All of these SEM micrographs indicated that these two-T_g samples were immiscible with a heterogeneous phase morphology.

However, homogeneous fractured surfaces with no resolvable SEM domain of IPNs of 50 wt % PCU/PMMA using the initiator BPO or redox initiator DMA/BPO were observed by SEM (Figure 13e,f). These observations confirmed the results of the DSC measurements, i.e. single-T_g samples exhibiting no resolvable SEM domains.

TEM observations give further support to the results from SEM and DSC measurements (Figure 14). The IPN of 50 wt % PCU/PMMA using the redox initiator DMA/BPO displayed no TEM resolvable domains even at higher magnifications up to 20 000. On the other hand, the sequential IPN of 80 wt % PCU/PMMA exhibited distinguishable black domains (0.2 μm) under TEM observation which were similar to those of the graft copolymer of PCU/PMMA.[23] The black areas indicate that PCU was strongly stained by OsO_4.[5]

Conclusions

Kinetics and phase morphology studies of SIPNs of PCU/PMMA and related materials have been carried out by means of DSC, SEM, and TEM. Kinetic parameters such as activation energy, reaction order, and conversion versus time and temperature of the SIPN have been studied via the DSC isothermal method with a computer-aided DSC data analysis program. The results from the DSC isothermal mode are in good agreement with those from the gravimetric experiment. The experimental evidence clearly showed that the phase morphologies of the SIPN of PCU/PMMA can be changed by changing the rates of the cross-linking reaction. A one phase SIPN of PCU/PMMA can be obtained if the cross-linking reactions of PCU and PMMA occur simultaneously. The data from the gravimetric experiments indicated that T_g's of the PCU/PMMA SIPNs increased with the increasing degree of conversion due to a higher degree of cross-linking.

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