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Effect of Molecular Weight and Molecular Architecture of PMMA on the Phase Morphology of Pseudo-IPN's of PCU/PMMA

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ABSTRACT: We have prepared pseudo-IPN's of cross-linked PCU and linear PMMA or four-arm star PMMAs of various molar masses of PMMA and various concentrations in weight percent PMMA. SEM and DSC investigations reveal that while the lower molar mass PMMA samples are phase-separated, the highest molar mass PMMAs of lower concentration in PMMA samples have a single T_g and no SEM-resolvable phase domains. We speculate on the formation of these metastable states as a consequence of reduction of molecular mobility with increasing molar mass.

1. Introduction

Simultaneous interpenetrating polymer networks (IPN's) and fully gelled grafted networks of poly(carbonate–urethane) (PCU) and poly(methyl methacrylate) (PMMA) recently have been prepared and characterized by us.[1,2] Over the whole composition range the full IPN's of PCU/PMMA are transparent solids with a single glass transition temperature (T_g) and no TEM-resolvable phase domains. On the other hand, the fully gelled, grafted network of PCU/PMMA (of the same composition as our IPN's) was phase separated with two T_g's and a phase domain of average linear dimension of about 4000 Å. Blends of linear PCU and linear PMMA chains are completely immiscible at all compositions, with two T_g's and phase domain sizes larger than 10 000 Å.

In this paper we describe the properties of the pseudo-IPN's of various compositions composed of linear or star PMMA's of varying molar mass dispersed in a cross-linked PCU matrix. These materials are prepared as solid films from a clear, homogeneous toluene solution, as described in the Experimental Section of this paper, by casting and drying the film in a Petri dish. This procedure does not allow us to control the kinetics of the earlier stages of the final sample preparation. Thus, we cannot comment to what extent and what time our sample arose by phase separation (spinodal decomposition and possibly even nucleation) from solvent containing reacting mixture or relatively solvent-free reacting mixture. We merely characterize by physical appearance, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) of the final, dried solid films.

We undertook these studies because we expected that the restricted molecular mobility of the highly entangled, dispersed PMMA chains and stars would tend to produce single-phase materials if the molar mass of the PMMA was sufficiently high and its weight fraction, w, was sufficiently low. This expectation was confirmed.

2. Experimental Section

(a) Materials. The raw materials employed and their descriptions are listed in Table I. The linear PMMA samples were purchased from Polysciences and Aldrich. The four-arm star PMMA samples were made by a group-transfer of MMA using a "core-first" method described elsewhere.[3] All of the PMMA samples were dried in a vacuum oven at 60 °C for 48 h before use. The linear hydroxyl-terminated polycarbonate (PC) was dissolved in toluene, then precipitated in petroleum ether, and dried at 50 °C in vacuum for 24 h. Toluene was refluxed over CaH_2 for 5 h, then distilled out in a nitrogen atmosphere, and stored over 4-Å molecular sieves. The aliphatic polyisocyanate, biuret triisocyanate (BTI), and dibutyltin dilaurate (DBTL) were used without further purification.

(b) Preparation of Pseudo-IPN's of PCU/PMMA. (PMMA is linear or a star polymer. PCU is cross-linked.) The linear or star PMMA was dissolved in toluene with stirring under a N_2 atmosphere. The concentration of the PMMA was about 5% by weight. Purified poly(carbonate diol) and BTI dissolved in toluene in separate bottles at a molar ratio of NCO/OH = 1.05 were then mixed together with the PMMA solutions. The mixture was stirred until all chemicals dissolved completely; then DBTL was added (0.2% (wt)) with vigorous stirring for 3 min. Then the solution was put into Petri dishes after degassing and heating at 60 °C for 8 h and 80 °C for 24 h. All operations were carried out under a nitrogen atmosphere. The product was dried under a vacuum at 80 °C for 24 h, and the resulting film was a transparent to translucent solid depending on the composition and molecular weight of the PMMA. The molecular weight between cross-links ($\bar{M}_c$) of the PCU networks was 850 (determined by the $\bar{M}_w$ of the PC).

3. Characterization

Differential Scanning Calorimetry (DSC). The glass transition temperatures were determined by DSC (DuPont 2910 DSC). The DSC was calibrated with 10 mg of indium standard sample before use. DSC measurements were carried out in 10-mg samples in a temperature range from −100 to +200°C at various rates of scanning. The first run was carried out at a scanning rate of 20 °C/min, followed by cooling down at 20 °C/min and heating again at 40 °C/min. Under a nitrogen atmosphere, three specimens were taken from each sample at different sample locations for DSC testing.

Scanning Electron Microscopy (SEM). Electron micrographs were obtained on a digital scanning microscope (DSM 940, Zeiss, West Germany). The preparation of specimens for SEM was as follows. The specimens were frozen under liquid nitrogen. They were fractured and mounted on a stub using silver paint, and subsequently, they were coated with gold (100 Å) on a Balzers 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 magnification employed in Figure 4 was 8500×.

Soxhlet Extraction. The Soxhlet extraction of the pseudo-IPN's of PCU/PMMA was carried out by using ethyl acetate as solvent for 24 h.

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Table I
Raw Materials Employed and Their Abbreviations

designation	name and description	source
PC (Duracab 120)	poly(1,6-hexanediol–carbonate), MW 850, hydroxyl functionality = 2.0	PPG Industries
BTI (Desmodur N-100)	biuret triisocyanate derived from hexamethylene diisocyanate, isocyanate functionality = 2.62	Mobay Chemical Co.
PMMA (linear)	poly(methyl methacrylate) (linear); $\bar{M}_w$ = 68 000, 330 000; polydispersities 2.80, 1.99	Aldrich Chemical Co.
PMMA (linear)	poly(methyl methacrylate) (linear); $\bar{M}_w$ = 33 500, 185 000, 2 300 000; polydispersities 1.10, 1.10, 2.2	Polysciences Inc.
PMMA (star)	poly(methyl methacrylate) (star), star PMMA, 4 arms; $\bar{M}_w$ 9100, 17 900, 35 700, 50 800; polydispersities 1.22, 1.22, 1.32, 1.22 (determined by GPC using PMMA standards)	
DBTL	dibutyltin dilaurate	Aldrich Chemical Co.
toluene	solvent grade	Aldrich Chemical Co.

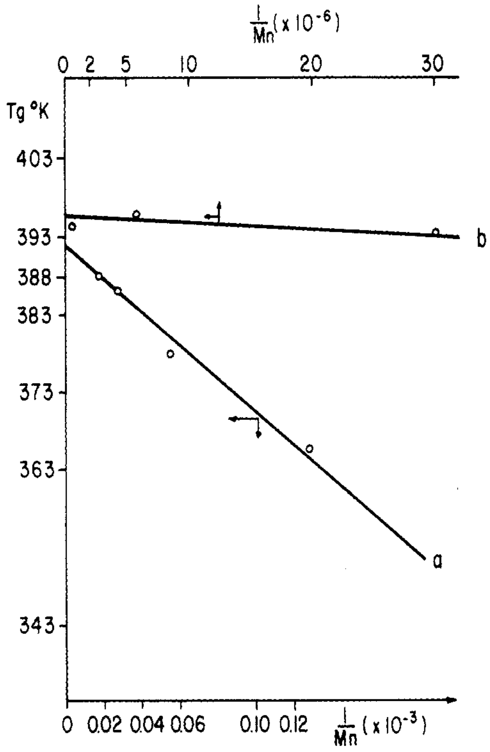

Figure 1. Plots of the T_g's of the linear and star PMMA samples versus $\bar{M}_n$: (a) star PMMA, slope 2.17 × 10⁵ K·g/mol; (b) linear PMMA, slope 1.10 × 10⁵ K·g/mol. This is consistent with expectations from eqs 1 and 2.

Table II
Glass Transition Temperatures (T_g's) of Pseudo-IPN's of PCU/PMMA (Linear and Star PMMA with Different Molecular Weights) in Which PCU Is Cross-Linked

PCU/PMMA (wt %)[a]	MW (PMMA)	T_g (°C)	
(a) 50/50	330 000	−43.2	105.1
70/30	330 000	−33.8	108.0
	68 000	−35.3	121.0
90/10	330 000	−22.5	
	68 000	−18.8	112.6
100/0		−36.0	
(b) 50/50	2 300 000	−13.3	29.6
70/30	2 300 000	−7.9	
90/10	2 300 000	−17.0	
(c) 50/50	50 800	−30.5	97.7
70/30	50 800	−32.8	97.8
90/10	50 800	−18.1	

[a] (a) Linear PMMA samples came from Aldrich. (b) Linear PMMA samples came from Polysciences. (c) Star PMMA.

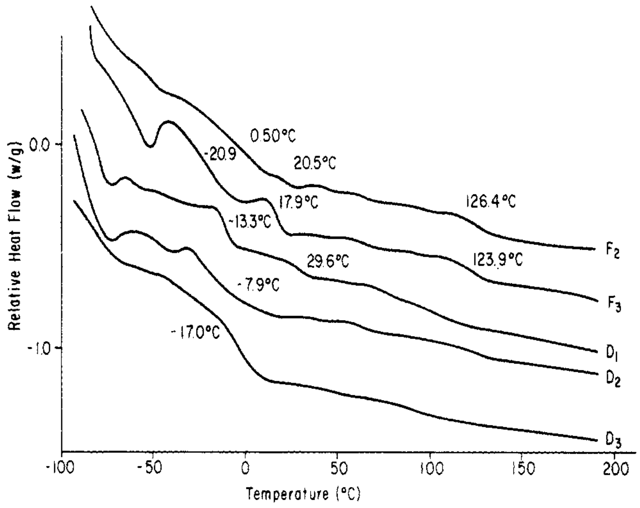

Figure 2. DSC traces of the pseudo-IPN's of PCU/PMMA with different $\bar{M}_w$'s of the linear PMMA. $\bar{M}_w$ 185 × 10³: (F$_2$) 30 wt % PMMA; (F$_3$) 10 wt % PMMA. $\bar{M}_w$ 2.3 × 10⁶: (D$_1$) 50 wt % PMMA; (D$_2$) 30 wt % PMMA; (D$_3$) 10 wt % PMMA.

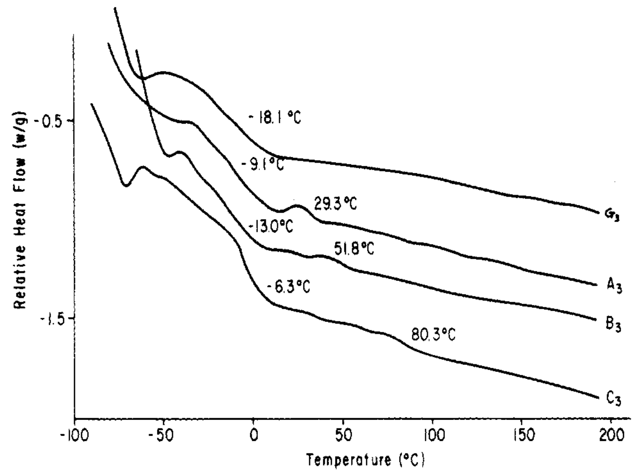

Figure 3. DSC traces of the pseudo-IPN's of PCU/PMMA whose PMMA is from four-arm star polymer with various $\bar{M}_w$'s at 10 wt % PMMA: (G$_3$) $\bar{M}_w$ 50.8 × 10³; (A$_3$) $\bar{M}_w$ 35.7 × 10³; (B$_3$) $\bar{M}_w$ 17.9 × 10³; (C$_3$) $\bar{M}_w$ 9.1 × 10³.

4. Results

Figure 1 shows the usual plot of the T_g's of the pure samples versus number-average molecular weight $\bar{M}_n$ or estimates thereof and its variation with architecture. The T_g's of the four-arm star PMMA samples were lower than those of linear PMMA samples, as expected from simple free volume considerations.[4] The glass transition temperatures of the four-arm star polymers, $T_{g,\mathrm{star}}$, of the linear polymers, T_g, and their infinite molar mass analogs ($T_g^{\infty}{}_{,\mathrm{star}}$ and T_g^{∞}, respectively) are related by

$$T_{g,\mathrm{star}} = T_g^{\infty}{}_{,\mathrm{star}} - 2K/\bar{M}_n \qquad (1)$$

$$T_g = T_g^{\infty} - K/\bar{M}_n \qquad (2)$$

with K = 1.1 × 10⁵ K·g/mol.

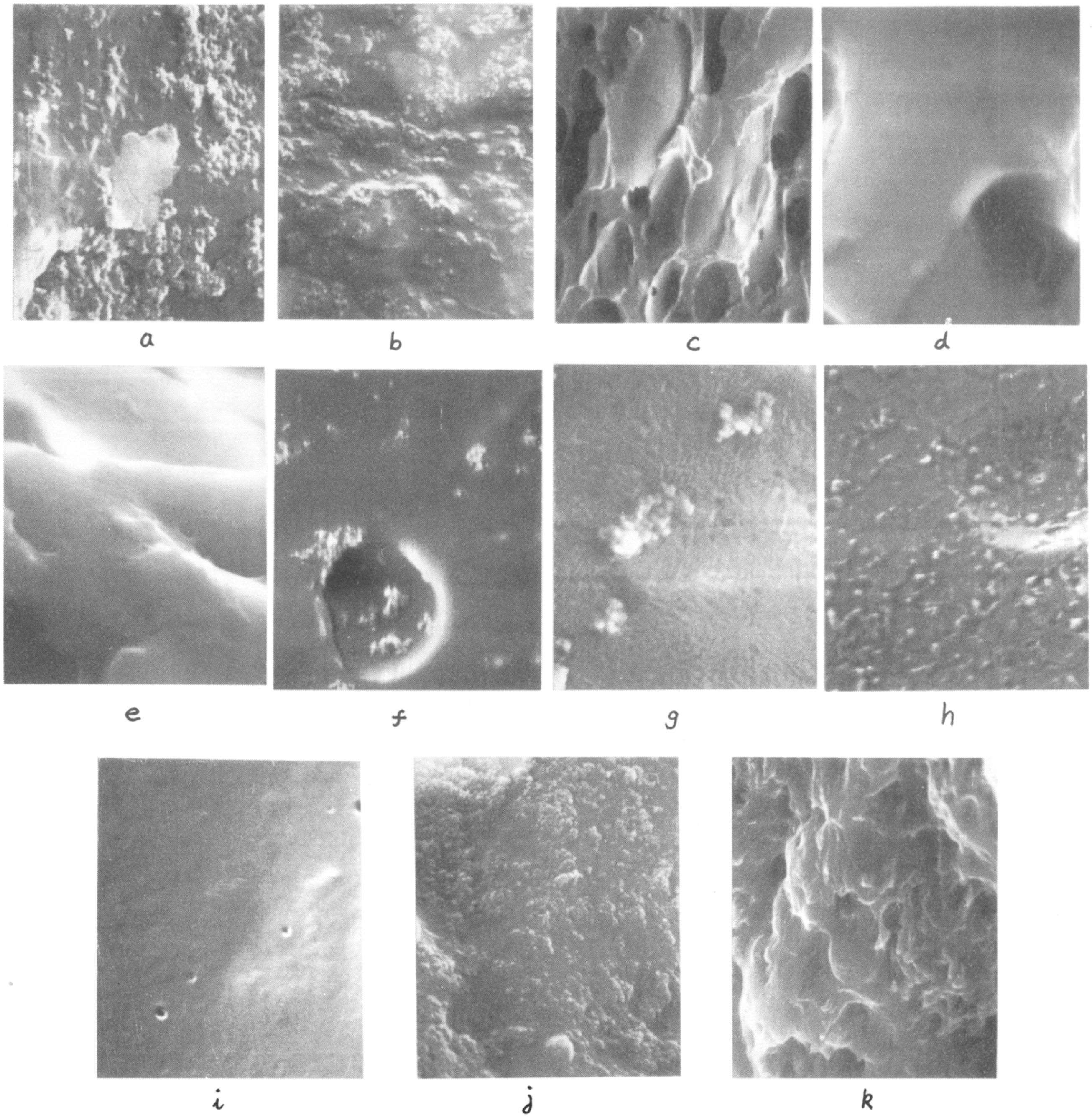

Figure 4. Scanning electron micrographs of the pseudo-IPN's of PCU/PMMA: (a) 10 wt % linear PMMA, $\bar{M}_w$ 33 × 10^3; (b) 10 wt % linear PMMA, $\bar{M}_w$ 185 × 10^3; (c) 50 wt % linear PMMA, $\bar{M}_w$ 2.3 × 10^6; (d) 30 wt % linear PMMA, $\bar{M}_w$ 2.3 × 10^6; (e) 10 wt % linear PMMA, $\bar{M}_w$ 2.3 × 10^6; (f) sample e after extraction; (g) 10 wt % star PMMA, $\bar{M}_w$ 9.1 × 10^3; (h) 10 wt % star PMMA, $\bar{M}_w$ 35.7 × 10^3; (i) 10 wt % star PMMA, $\bar{M}_w$ 50.8 × 10^3; (j) 30 wt % star PMMA, $\bar{M}_w$ 50.8 × 10^3; (k) 50 wt % star PMMA, $\bar{M}_w$ 50.8 × 10^3.

Table II gives the T_g's of the pseudo-IPN's of PCU/PMMA with linear and star PMMA. It can be seen that the pseudo-IPN's of PCU/PMMA with a low molecular weight of linear PMMA are phase separate at all compositions studied; however, the pseudo-IPN's of PCU/PMMA with higher molecular weights of linear and star PMMA possess a single T_g of 10%, 30% and 10% PMMA by weight, respectively.

Figure 2 shows the DSC spectra of the pseudo-IPN's of PCU/PMMA whose linear PMMA was purchased from Polysciences Inc. The PMMA samples had a narrower MW distribution. It was shown that the pseudo-IPN's of PCU/PMMA with the highest $\bar{M}_w$ (2.3 × 10^6) possess a single phase with one T_g at 10% and 30% (wt) PMMA compositions. The samples are transparent solids. However, the pseudo-IPN's of PCU/PMMA with lower $\bar{M}_w$ (185 × 10^3) have several transition temperatures of which the highest one is almost that of the T_g of pure PMMA. The lowest one is close to the T_g of PCU. The middle T_g's may reflect, when it occurs, entanglement of the PMMA chains with the PCU network at higher concentrations and lower molar masses.

The pseudo-IPN's of PCU/PMMA made from 10 wt % of the four-arm star show a larger inward shift of the T_g's, as can be seen in Figure 3. This narrowing increases with increasing molar mass. It is tempting to associate this with a tendency toward higher miscibility of the PMMA even in the multiple-T_g, phase-separated samples. Finally, the sample made from the star of molar mass of 50.8 × 10^3 exhibited only one T_g.

Scanning electron microscopy (SEM) for the fractured surface of the pseudo-IPN's of PCU/PMMA essentially confirms the results obtained by DSC measurement (Figure 4). The pseudo-IPN's of PCU/PMMA with a

Table III
Results of Soxhlet Extraction of the Pseudo-IPN's of PCU/PMMA

sample	PCU/ PMMA (wt %)	MW (PMMA)	wt % PMMA remaining	physical properties	
				before extraction	after extraction
pseudo-IPN (linear-PMMA)	70/30	2.3×10^6	4.2	one T_g, transparent, no SEM domain	two T_g, opaque, SEM domain 0.2–0.8 μm, softer
	90/10	2.3×10^6	5.0		
	90/10	330×10^3	4.0	one T_g, transparent, no SEM domain	two T_g, translucent, softer
	90/10	33×10^3	1.2	two T_g, translucent, SEM domain 0.5–1.0 μm	one T_g, transparent, softer
(four-arm star PMMA)	90/10	50.8×10^3	7.7	one T_g, transparent, no SEM domain	one T_g, transparent
blend	70/30	2.3×10^6	none		

higher MW of linear or star PMMA appear to have a homogeneous surface with no resolvable phase domains even at 8500× magnification. Thus, single-T_g samples appear to possess one phase, and multiple-T_g samples, to possess more than one phase.

The Soxhlet extraction results are summarized in Table III.

5. Discussion

The pseudo-IPN's of the linear or star PMMA are solids in which the PMMA coils are presumably entangled with the PCU network coil, consistent with the usual "blob" view of solid polymers.[5] In effect they are a form of polymeric rotaxanes. We have already pointed out that we have no control on the initial stages of phase separation. There is no complete theory of such separation except for limiting situations.[6] We speculate that among other factors, the molecular mobility of the PMMA chains or star must play a controlling role. In either the solid or dense solution the motion of these polymers is some form of reptation. For linear polymers the reptation mobility falls within the inverse second power of the molar mass, and for stars it falls even more strongly (possibly exponentially with molar mass).[7] This suggests that for sufficiently high molar mass, metastable morphological states could be reached in which the phase separation has not occurred even for time periods on the order of months. We believe that this accounts for the single-T_g samples which reveal no phase separation in the SEM micrographs. This is our principal conclusion. To confirm this strictly, we would require extensive X-ray and neutron scattering kinetic studies.[8]

The results of the Soxhlet extraction are consistent with our speculation. The extraction seriously modifies the metastable equilibrium of the highest molar mass linear PMMA and star PMMA (at highest $\bar{M}_w$) samples of pseudo-IPN's, producing now some evidence of phase separation (two T_g's). We note that in these cases the extraction also has not removed all of the PMMA, as might be expected from the small molecular mobility of these polymers in Table III (cf. also Figure 4g in comparison with Figure 4i). It was noted that the highest amount of the star polymer remaining in the pseudo-IPN after extraction may be a reflection of the possible exponential decay of the mobility of a star polymer as compared to the algebraic decay proportional to $\bar{M}_n^{-2}$ for linear polymer. We have previously shown that the linear blends of lower molar mass PMMA and linear PCU can be fully separated.[2]

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References and Notes

(1) Frisch, H. L.; Zhou, P.; Frisch, K. C.; Xiao, X. H.; Huang, W.; Ghiradella, H. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1031.
(2) Zhou, P.; Frisch, H. L. *J. Polym. Sci. Polym. Chem. Ed.* **1992**, *30*, 2577.
(3) Zhu, Z.; Rider, J.; Yang, C. Y.; Gilmartin, M. E.; Wnek, G. E. Preceding article in this issue.
(4) Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman and Hall: London, 1991; p 300.
(5) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1970.
(6) Binder, K.; Frisch, H. L. *J. Chem. Phys.* **1984**, *81*, 2126.
(7) Grosberg, A.; Frisch, H. L. Unpublished results.
(8) Daoud, M.; Brulet, A.; Zhou, P.; Frisch, H. L. Initial neutron scattering studies are under way, unpublished results.

Registry No. PMMA, 9011-14-7; (Desmodur N100)(Duracarb 120) (block copolymer), 144634-56-0.