Linear chains in networks with monodisperse molecular weight subchains

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Monodisperse linear polytetrahydrofuran (PTHF) chains with unreactive end groups were mixed with PTHF chains with reactive ends. The concentration of the linear unreactive chains was dilute, approximately 3 wt%. The phase behaviour as well as the single chain conformation of the unreactive chains was investigated after the reactive chains were end-linked via either a tetrafunctional crosslinker or a free radical polyaddition reaction. The results were found to depend strongly on the difference in the molecular weights between the reactive chains and the unattached linear chains.

(Keywords: polytetrahydrofuran; network; end-linking; phase separation; chain contraction)

INTRODUCTION

The effect of crosslinking the solvent molecules on the phase behaviour of the dissolved and unattached linear chains (the solute) is an interesting problem. From the theoretical point of view based on mean field approximation, the network can be regarded as a homogeneous elastic medium and crosslinks are expected to inhibit phase separation[1]. This is because the segregated linear chains will perturb their surrounding network chains from their most probable configurations, and will inevitably result in additional elastic energy. This elastic energy acts as a stabilizing force against phase separation.

The experimental results, however, point in the opposite direction. Most significant are the results of recent work on poly(vinylmethylether) (PVME)/polystyrene (PS) blends. The results indicate that crosslinking the polystyrene matrix makes the blend more susceptible to phase separation[2-4]. In other words, crosslinking of the matrix or the solvent tends to destabilize the blend. One possible explanation could be that the distribution of the crosslinks in the system studied was inhomogeneous, and the linear chains tended to migrate to where the crosslink density was low. To examine this conjecture, the crosslinkable solvents used in the present work are monodisperse polytetrahydrofuran (PTHF) chains with either diallyl end groups or methyl methacrylate (MMA) ends. By end-linking chains with a narrow molecular weight distribution the problem of heterogeneity in the crosslink density can be minimized. However, one cannot eliminate the formation of topological defects in networks by using monodisperse subchains. The unreactive PTHFs also have monodisperse molecular weight. The difference in molecular weight between the network chains and the unattached linear chains is the major experimental variable for this work.

The above discussion regarding the elastic energy should not be confused with the well known relation between the crosslink density and the swelling ratio in network–small molecular solvent systems. In these cases swelling equilibrium is reached as the osmotic force which tends to expand the network is counterbalanced by the elastic force which tends to contract the network[5]. A high crosslink density leads to a low equilibrium swelling ratio. Crosslinking of polymer in solutions can result in macrosyneresis, i.e. the expelling of solvent molecules from the network. Since the equilibrium swelling ratio depends strongly on crosslink density, local variation in crosslink density will result in microsyneresis[6], an uneven distribution of the solvent molecules inside a crosslinked material. It is noteworthy that for either macrosyneresis or microsyneresis to occur the solvent content is above the equilibrium swelling ratio in a macroscopic or a local scale, respectively. Direct evidence of microsyneresis can be obtained from various scattering measurements such as light, X-ray or neutron scattering. Some extra scattering intensities often appear in the low angle region, and this observation has been attributed to the non-uniformity of the crosslink density in the sample. More important is the observation that its contribution decreases significantly as the network is deswelled[7]. In other words, the extent of microsyneresis diminishes as the solvent content in the sample decreases.

In this work the solute (uncrosslinkable chains) content of all the crosslinked samples is 3% and the

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equilibrium swelling ratio of the most tightly crosslinked sample in THF is 60%. Microsyneresis is unlikely to occur in samples with such a low solvent content, at least not in the case of small molecule solvents. The results of this work will demonstrate that the size of the solute molecules relative to the mesh size of the network is an important factor determining the 'microsyneresis' or phase separation. As the solute molecule is about the same size as the subchain between crosslinks, no microsyneresis or phase separation was observed. One does not expect to observe microsyneresis at 3% solvent content if the solvent molecules are smaller than the subchain. Throughout this work, the size or the molecular weight of the solute was kept fixed while the subchain size varied. As the crosslink density or the subchain size went below that of the solute molecule, phase separation occurred. The experimental findings regarding phase separation should not be confused with that in network–small molecule solvent systems where the subchain size can never be equal to or smaller than the solvent.

The other main purpose of this work is to examine the conformation of individual linear chains dissolved in a crosslinked matrix. Some theoretical work[8–10] has predicted that the presence of random impenetrable obstacles will cause some contraction of the embedded linear chains. The extent of contraction depends on the molecular weight of the solute and the density of the obstacles. One could regard the crosslink points as impenetrable obstacles due to the repulsive interaction between the linear chain and the crosslinks, at least in terms of their hard core repulsion which must be greater than that between the linear chains and the linear portion of the network chains. The population of these obstacles or junctions is controlled by the molecular weight of the solvent chains before crosslinking.

EXPERIMENTAL

Materials

For all the small-angle neutron scattering (SANS) samples the linear unreactive PTHF are blends of deuterated and protonated samples, and the network PTHF are all protonated. The synthesis of the diallyl-terminated PTHF with narrow molecular weight distribution was carried out according to the method of Smith and Hubin[11]. The PTHF chain with methyl methacrylate ends was obtained from ALCOLAC Incorporated*. The ends of the unreactive species were capped with butanol. The gas-permeation chromatography (g.p.c.) results of the PTHF samples based on polystyrene equivalent molecular weight are listed in *Table 1*, and these values are believed to be greater than the true ones. This uncertainty in molecular weight does not present a major problem since the relative difference between the solvent and the solute molecular weights is the main factor affecting the results to be discussed.

Pentaerythritol tetrakis(3-mercaptopropionate) was used as the crosslinker for SH1, SH2 and SH3, the functionality of which was determined to be 3.8[12]; a stoichiometric amount was used for all samples. The crosslink reaction was initiated with benzopinacole, which stayed quite stable until heated above 80°C. The concentration of the initiator was 0.2% of the sample weight. For SH4 benzoperoxide at 0.5% of the sample weight was used as the initiator.

For each sample, distilled THF equal to the sample weight was added to ensure a homogeneous mixing of the starting materials. Twenty minutes after the starting materials were dissolved vacuum was applied to remove all THF, followed by raising the temperature to 80°C. All the samples stayed at this temperature in vacuum for 4 days to complete the cure. Nine samples were studied, their compositions are given in *Table 2*. Sample 1 was a blend of matched molecular weight protonated and deuterated PTHF for determining the single chain form factor in its unperturbed state. The other four pairs of samples were prepared so that the single chain form factor of the linear chain while dissolved in crosslinked matrix could be extracted.

SANS measurements

The 8 m SANS facility in the Reactor Division of the National Institute of Standards and Technology was used. The sample temperature was kept at 60°C throughout the measurement to avoid crystallization of the PTHF chains. The wavelength of the incident neutrons was set at 12 Å, and the q range covered was from 0.005 to 0.08 $Å^{-1}$, where q denotes the magnitude of the scattering vector as usually defined. After subtraction of the incoherent component and the empty cell background, the scattered neutron intensity was reduced to its absolute scale using a silica gel sample as a secondary calibration standard.

Table 1 Molecular weight of PTHF polymers (polystyrene equivalent)

	M_n	M_w
LD	14 300	16 300
LH	14 600	16 800
SH1	12 400	16 800
SH2	1 200	1 400
SH3	1 500	1 700
SH4	780	1 000

LD, linear deuterated chains with their ends capped by butanol groups; LH, linear protonated chains to be blended with LD for determination of the single chain form factor; SH, protonated solvent chains; SH1, SH2 and SH3 are diallyl terminated and SH4 has methyl methacrylate ends

Table 2 Compositions (wt%) of the samples used in SANS measurements

Sample designation number	LD	LH	SH1	SH2	SH3	SH4
1	8	92	–	–	–	–
2	3	–	97	–	–	–
3	2	1	97	–	–	–
4	3	–	–	97	–	–
5	2	1	–	97	–	–
6	3	–	–	–	97	–
7	2	1	–	–	97	–
8	3	–	–	–	–	97
9	2	1	–	–	–	97

*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply necessarily the best available for the purpose

RESULTS AND DISCUSSION

The SANS result from sample 1 and its fit to a Debye function are given in *Figure 1* showing a good fit between the SANS data and the Debye function. This suggests that PTHF molecules are flexible coils under the measurement condition used in this work. The contrast factor per repeat unit between the protonated and the deuterated PTHF was 0.57 cm^{-1}, denoted as K_n, based on a polymer density[13] of 0.982 g cm^{-3}. The extrapolated zero angle intensity $I(q\rightarrow 0)$ of 7.2 cm^{-1} gives a degree of polymerization (DP) of 170, which is significantly less than the g.p.c. results of *Table 1*, by a factor of ~26%. The radius of gyration (R_g) from the Debye function fit was 43 Å. Based on a literature constant[13] relating molecular weight to R_g, the calculated molecular weight was 12800 or $DP=185$, which was quite close to the $I(q\rightarrow 0)$ value of 170. The value ϕ^*, the overlapping concentration for the PTHF was calculated to be 7.6 vol% based on $DP=170$ and $R_g=43$ Å. Hence the unreactive PTHF concentrations in samples 2–9 were all in the dilute region. Throughout this paper, the scattered intensities were normalized by a factor $\phi_d(1-\phi_d)$, where ϕ_d is the d-PTHF concentration, in order to facilitate the comparison of SANS results from samples different in the d-PTHF content. The scattered intensities so normalized have units of cm^{-1}. In order to reduce the single chain form factor from sample pairs that differ in the H–D ratio but are identical in the total linear chain content, some of the scattered intensities were further reduced by the contrast factor, K_n, of 0.57 cm^{-1}, and the reduced intensities were dimensionless.

The SANS results of samples 1 and 3 are given in *Figure 2a*; the crosslinking of h-PTHF resulted in a minor increase of SANS intensities in the low q region even though the molecular weights of the H and D chains were almost matched. This increase suggests some demixing between the network and the dissolved linear chains. This result is also presented in *Figure 2b* in terms of $1/I(q)$ *versus* q^2, or the Zimm plot. Based on *Figure 2b* it is obvious that the minimum q range covered in this work was so limited that a reliable zero q extrapolation cannot be obtained, hence no definitive conclusion regarding the extent of demixing can be drawn from this figure.

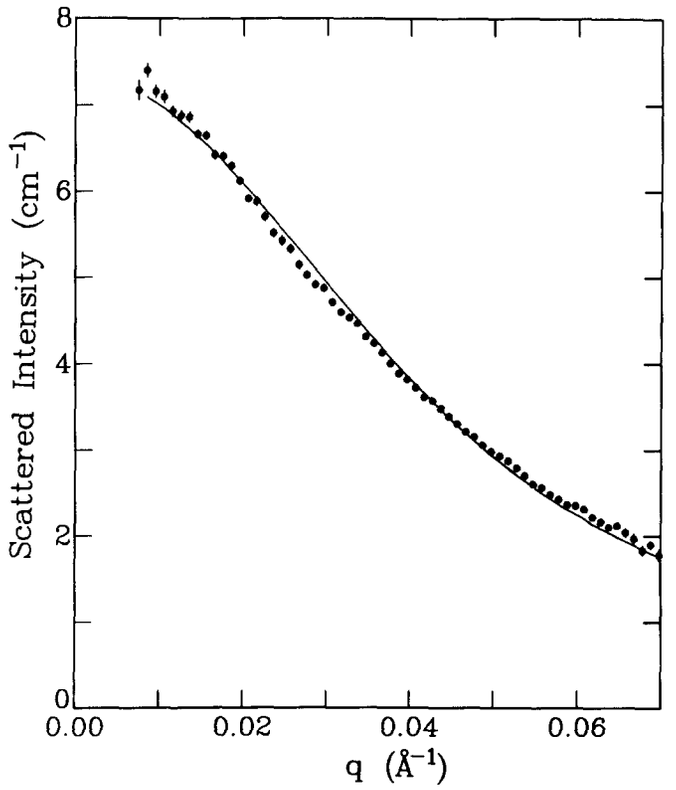

Figure 1 SANS results from a linear PTHF blend containing 8 wt% deuterated chains. (——) Fit of a Debye function with R_g of 43 Å and degree of polymerization of 170

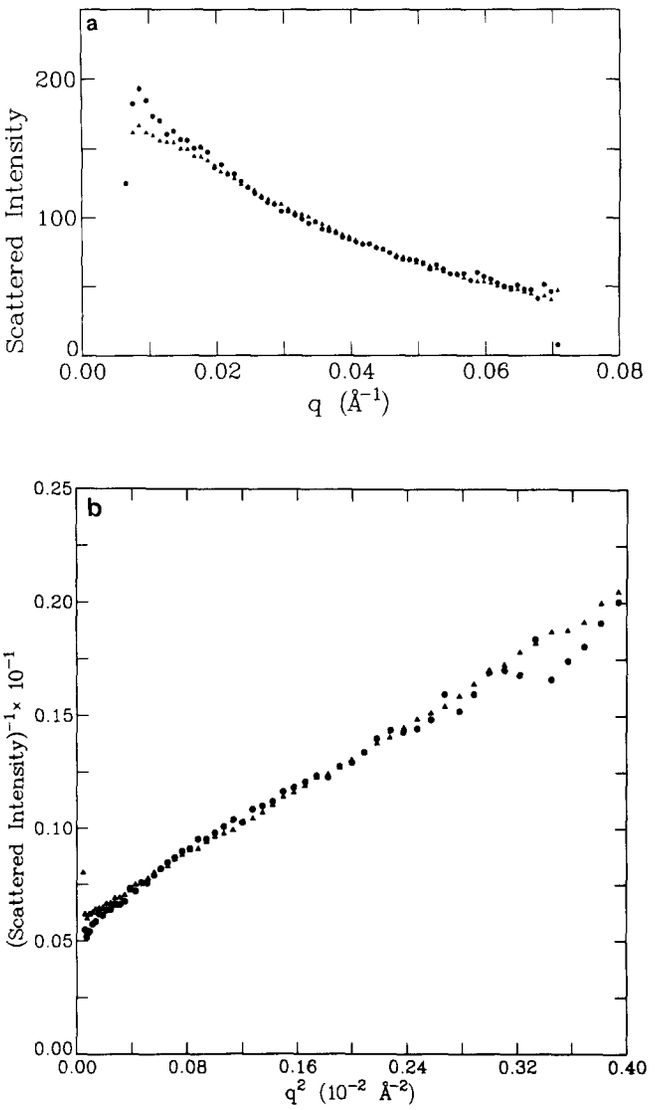

Figure 2 (a) SANS result from a sample containing 3 wt% linear deuterated PTHF embedded in crosslinked protonated PTHF (●). The molecular weights of the h-PTHF and the d-PTHF are 12400 and 14300, respectively. The results of *Figure 1* (▲) are presented for reference. (b) Same results as in (a) presented in a Zimm plot

The SANS results of samples 1, 5, 7 and 9 are given in *Figure 3*. The extrapolations of the data from samples 5, 7 and 9 towards zero q all pass through zero; this implies that the demixing is extensive in all three samples and phase separation has already taken place.

The SANS result of sample 8 before cure, i.e. from the mixture of the linear d-PTHF and SH4 without any initiator, is given in *Figure 4* together with the SANS result of sample 1. As shown in *Figure 4* the inverse of the SANS intensities of the uncured sample is greater

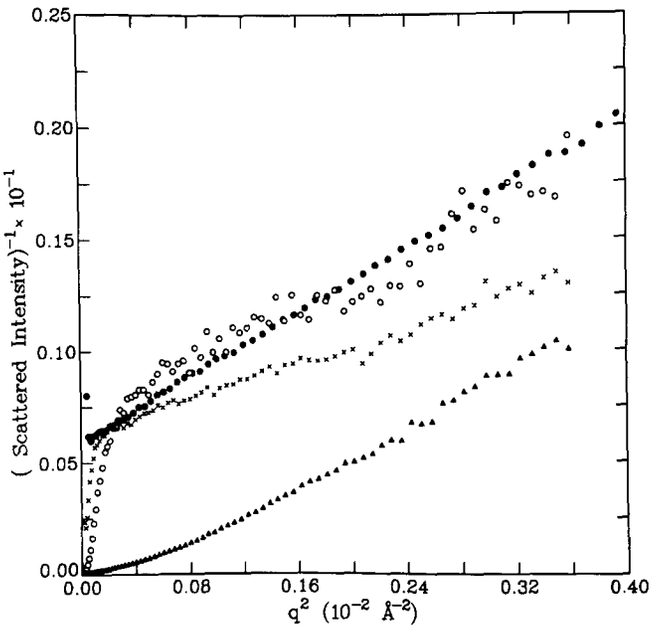

Figure 3 SANS results in the Zimm plot of 3 wt% linear d-PTHF embedded in crosslinked h-PTHF with the following compositions: (○) $M_n = 1462$ with diallyl ends; (×) $M_n = 1181$ with diallyl ends; (▲) $M_n = 780$ with MMA ends. The result from the linear PTHF blend (●) is also presented as reference

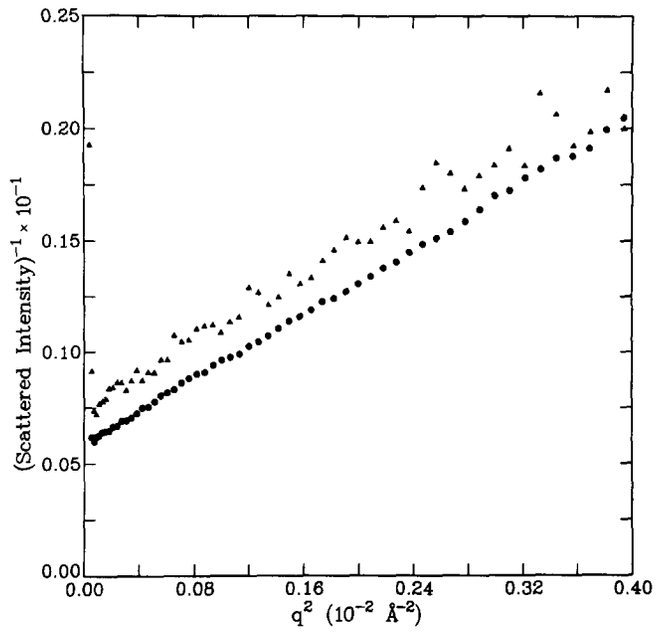

Figure 4 SANS results from a sample of 3 wt% linear d-PTHF dissolved in linear h-PTHF with MMA attached to both ends (▲). The result from *Figure 1* (●) is also given as reference

than that of the linear long chain blend (sample 1). The SANS values of $1/(I(q \to 0)$ from the uncured and the linear blend are 0.068 and 0.0556, respectively. This difference can be accounted for using the result (equation (1)) derived from a random phase approximation (RPA) scheme[14]:

$$\frac{K_n}{I(q)} = \frac{1}{\phi_1 N_1 P_1(q)} + \frac{1}{\phi_2 N_2 P_2(q)} - 2\chi \qquad (1)$$

where ϕ_1, N_1 and $P_1(q)$ denote volume fraction, degree of polymerization and normalized single chain form factor of d-PTHF; ϕ_2, N_2 and $P_2(q)$ denote the same quantities for h-PTHF in the case of sample 1 as listed in *Table 1*, and for SH4 in the case of the uncured mixture of d-PTHF and SH4; χ stands for the Flory–Huggins interaction parameter and is assumed to be negligibly small. The difference in the $1/I(q)$ observed in *Figure 4* can be accounted for almost entirely from the difference in the values of N_2. This indicates that the value of χ between d-PTHF and SH4 must be small. The MMA content in SH4 is ~25%, hence the value of χ between d-PTHF and MMA must also be small. This is an important point and it will be discussed in detail in a later part of this work.

The single chain form factor, $NP(q)$, reduced from the SANS results of the four sample pairs that differ only in their D/H ratios are given in *Figure 5*. The scheme to extract $NP(q)$ from these pairs can be outlined by equation (2). This equation can be rationalized from the fact that the scattering intensity involves only pair correlation, it must be a polynomial in ϕ of order 2.

$$I(q)/K_n = \phi_d NP(q) + \phi_d^2 X(q) \qquad (2)$$

ϕ_d denotes the concentration of the deuterated chain as before, and the interchain term $X(q)$ depends only on the total concentration of the linear unattached PTHF, not just the deuterated species. Therefore $X(q)$ values for sample 3 and sample 4 are identical and so on for other pairs. The results of $X(q)$ have no importance for the subject covered in this work, hence will not be reported. One can easily remove $X(q)$ by an appropriate subtraction of $I(q)$ values from samples 3 and 4. For all of the crosslinked materials there is a large increase in the SANS intensities in the low q region; this points to a large increase in the interchain contribution or $X(q)$ upon crosslinking. The reduction procedure to obtain the form factor then amounts to a subtraction of two large numbers to obtain a quantity which is a few orders of magnitude smaller. Consequently, the uncertainty of the result is great especially in light of the possibility that the extent of phase separation may not be strictly identical within the sample pairs, and the subtraction will not necessarily cancel out the quantity $X(q)$. Due to the large uncertainty of the results on *Figure 5*, especially in the low q region,

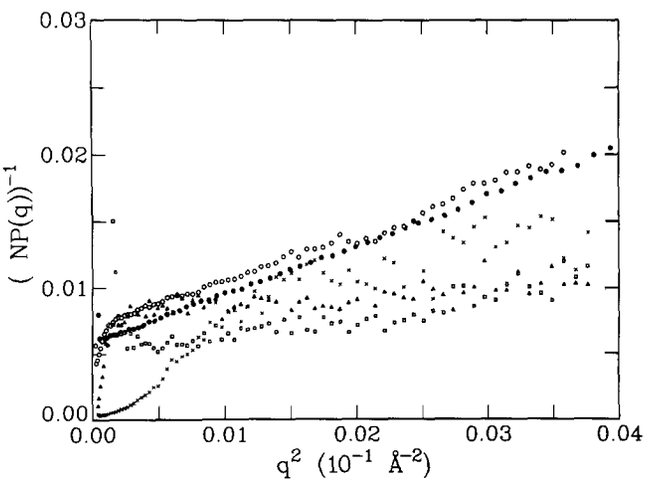

Figure 5 Single chain form factors of linear d-PTHF embedded in crosslinked h-PTHF with the following compositions; (○) $M_n = 12\,394$ with diallyl ends: (▲) $M_n = 1462$ with diallyl ends; (□) $M_n = 1181$ with diallyl ends; (×) $M_n = 780$ with MMA ends. The results of the linear PTHF blend (●) are also given as reference

Table 3 Results of linear fit of the data from *Figure 5* in the intermediate q region

Major content	Intercept ($\times 10^{-2}$)	Slope	N	R_g (Å)
LH	0.556	3.44	180	43.1
SH1	0.687	3.58	146	39.5
SH2	0.536	0.993	187	23.6
SH3	0.580	0.804	172	20.4
SH4	0.722	1.69	138	26.5

the rest of the discussion will be based on the data greater than $q^2 = 0.0005$ Å^{-2} named as the intermediate q region. Even in the intermediate q region there is a substantial scatter of the data.

The most striking feature in *Figure 5* is that the intensities in the intermediate q region for those samples containing SH2, SH3 and SH4 are higher than that of the linear blend. This indicates that the local segmental density of individual linear chains becomes enhanced when surrounded by a crosslinked matrix. One can calculate the radius of gyration R_g from the slope and the intercept of the data on *Figure 5*. The results are given in *Table 3*. The degree of polymerization N is the inverse of intercept.

The uncertainty in the estimated value of R_g must be large due to the scatter of data in the intermediate q region. Nevertheless, the results do point to a decrease in the R_g of individual linear chains once embedded in crosslinked matrix. The amount of decrease in R_g is as high as 50%. The fact that the values of $I(q \rightarrow 0)$ listed in *Table 3* do not converge to a single value attests to the large uncertainty of the results.

A precise determination of the single chain conformation of the linear PTHF using SANS has its intrinsic difficulty; the concentration of the linear chains needs to be highly dilute to ensure that the linear chains are surrounded by the crosslinked matrix instead of by other linear chains. This low concentration of d-PTHF leads to a small first term of equation (2). Unfortunately, crosslinking results in a phase separation of the linear chains, hence a significant increase in $X(q)$, the second term of equation (2). To extract single chain form factors thus involves the subtraction of two large numbers to obtain a number much smaller. Compounding the problem further, even when the linear chain concentration was kept in the dilute region as in this study, the local concentration of the linear chains must be enhanced due to phase separation. For the extreme case where one of the phases is largely composed of linear chains and the size of the phase is much larger than R_g, the conformation of the linear chains is expected to be restored to that of a Gaussian coil. This could be the case for samples 8 and 9 where massive phase separation is evident in the results shown on *Figure 3*. The value of R_g in *Table 3* for samples with SH4 matrix is higher than that from samples with SH2 and SH3. However, too much emphasis should not be placed on this observation due to the amount of data scatter. Work on samples with labelled free chains of polydimethylsiloxane dissolved in non-deuterated networks has been reported, and the molecular weights of the free chains in the subchains were identical[18]. No free chain segregation was observed. Work has now been extended to networks with tighter crosslinked densities; phase separation of the free chains was observed but not the collapse of the free chains[19].

One final point to be addressed is the compatibility of the starting materials used in this work. Deuterated and protonated PTHFs are compatible at least for the molecular weights used. Their compatibility is evident from the results shown in *Figure 1*; the SANS intensities of a D/H blend follow the Debye function. Deuterated PTHF and SH4, which is a low-molecular-weight h-PTHF with methyl methacrylate ends, are also compatible, as shown by the results in *Figure 4*. The only starting material which cannot be readily mixed with the others is the crosslinker, pentaerythritol tetrakis(3-mercaptopropionate). The sample preparation procedure used in this work involved the use of THF as solvent to dissolve all the starting components. After evaporating the solvent a clear solution was obtained. It is likely that part of the crosslinker had already reacted with the h-PTHF and that the reactant acted as a compatibilizer. The incompatibility between the crosslinker and the PTHF raises a problem regarding the chemical origin of the incompatibility between the network and the embedded linear chains. The molecular weight of the crosslinker is 440 which is comparable to the molecular weights of both SH2 and SH3. Consequently the concentration of crosslinker in the matrix is not negligibly small. Thus, it is reasonable to question the origin of the phase separation in samples containing either SH2 or SH3; part of the incompatibility may be due to the presence of the crosslinker in the network. However, the results of samples containing SH4 demonstrate conclusively that crosslinking is responsible for the massive phase separation observed. Since this is the sample where SANS intensities from the uncured mixture are also available, a direct comparison can be made between the uncured and the cured ones. In this case the uncured sample was prepared by simply mixing SH4 and LD1 without adding the initiator; at the SANS measurement temperature of 60°C no crosslinking reaction occurred. For the samples containing SH1, SH2 and SH3, the crosslinker is incompatible with the rest of the starting materials. As stated earlier, partial reaction with the PTHF was necessary to form an optically clear solution. Hence, no SANS results were available for those samples in the uncured state. In the rest of this paper only the results from SH4-containing samples will be used to delineate the relation between crosslinking and phase separation.

Crosslinking results in the addition of elastic energy as well as changes in the entropy of mixing. Since the contribution of elastic energy to phase separation is the main subject of this study and is uncertain at this point, the contribution from the entropy of mixing will be examined first with the hope of quantifying its effect on phase separation. Thereafter, its contribution can be isolated and a definitive conclusion regarding the elastic energy contribution to phase separation can be drawn based on the experimental observations.

SH4 can be considered as a triblock copolymer of MMA–hPTHF–MMA; hereafter d-PTHF, h-PTHF and MMA will be designated as components 1, 2 and 3 respectively. After cure, SH4 is converted into a network made of linear PMMA chains connected by h-PTHF branches. The degree of polymerization of PMMA chains is large and can be considered as infinite for the present purpose. There is one h-PTHF branch per MMA repeat unit on the PMMA chains. The effect of crosslinks on the entropy of mixing can be estimated by examining its

effect on χ_c, the critical Flory–Huggins interaction parameter beyond which phase separation occurs. Based on the RPA theory, the values of χ_c before and after the cure can be estimated readily as follows.

The criterion for phase separation in terms of the separation of linear d-PTHF chains can be set as the scattering intensities diverge at zero q. For a mixture of block copolymers and homopolymers[15], the criterion can be written as

$$\lim_{q\to 0}[X_T(q)-(\chi_3+\chi_2)X_x(q)][1-\chi_1 X_3(q)]$$
$$+X_1(q)[1-\chi_3 X_3(q)-\chi_2 X_2(q)+\chi_2\chi_3 X_x(q)]=0 \quad (3)$$

where $\chi_1=\chi_{12}+\chi_{13}-\chi_{23}$, a typical definition for the interaction parameters in ternary systems. χ_2 and χ_3 are defined in a similar way.

Results similar to equation (3) but in a different form can also be found elsewhere[16]. X_T denotes the intrachain or intranetwork correlation function, more explicitly it stands for

$$X_T=X_{22}+X_{33}+2X_{23} \quad (4)$$

X_x is the cross-correlation function defined as

$$X_x=X_{22}X_{33}-X_{23}^2 \quad (5)$$

where X_{22} is the self-correlation function of component 2 and the remaining X_{ij}s have similar meanings. By further assuming that $\chi_{23}=\chi_{31}=\chi$ and $\chi_{12}=0$, implying that the isotope effect between h-PTHF and d-PTHF is negligibly small, equation (3) can be simplified as

$$X_T-2\chi X_x+X_1(1-2\chi X_3)=0 \quad (6)$$

Through a simple algebraic calculation similar to that carried out elsewhere[17], the expression of χ_c for the mixture of MMA–hPTHF–MMA and d-PTHF is

$$2\chi_c=\frac{\phi_1 N_1+(\phi_2+\phi_3)(N_2+2N_3)}{2\phi_1 N_1\phi_3 N_3} \quad (7)$$

and for the cured materials

$$2\chi_c=\frac{(\phi_2+\phi_3)(N_2+2N_3)}{2\phi_1\phi_3 N_1 N_3} \quad (8)$$

The above results were based on an approximation of monodisperse molecular weights for all the components. Using the values for ϕ_i and N_i from *Tables 1* and *2*, the values of $2\chi_c$ are found to be 6.8 and 4.5 per MMA unit for the uncured and the cured materials, respectively. The above calculation indicates that crosslinking does make the material more susceptible to phase separation without considering the elastic energy contribution. Now the critical question is the magnitude of χ between MMA and PTHF; if its value is above 4.5 then the observed phase separation can be attributed solely to the reduction of the entropy of mixing.

The upper limit of χ between MMA and PTHF can be estimated as follows. We observed that 3 vol% PTHF of molecular weight 15 000 can be readily dissolved in MMA at room temperature. Equation (7) can be modified for a binary mixture of MMA and linear PTHF by taking both N_2 and ϕ_2 to zero and by replacing $2N_3$ as N_3, implying the replacement of a MMA–hPTHF–MMA triblock copolymer by a MMA unit, one has

$$2\chi_c=\frac{\phi_1 N_1+\phi_3 N_3}{\phi_1\phi_3 N_1 N_3} \quad (9)$$

The above result is identical to the RPA result of equation (1) for binary blends of linear polymers[14]. By substituting the appropriate values for N_1, N_3, ϕ_1 and ϕ_3 the value of $2\chi_c$ is 1.25 and its true value must be lower than this. The results of *Figure 3* also suggest a small χ between MMA and PTHF. Since the value of $2\chi_c$ for the cured material is 4.5, the massive phase separation observed in samples 8 and 9 cannot be attributed to the decrease of the entropy of mixing alone; the elastic energy must also contribute to the phase separation.

CONCLUSIONS

Crosslinking of PTHF chain of monodisperse molecular weight results in demixing of the dissolved linear PTHF chains. The extent of demixing depends on the difference in the molecular weights between the linear PTHF and the network chain between crosslinks. Demixing was observed in every sample tested even when their molecular weights were in the same range. As the molecular weights of the subchains were ~10% of the dissolved linear chains, crosslinking gives rise to phase separation. Note that the equilibrium swelling ratio of these crosslinked PTHF samples in THF is at least an order of magnitude greater than 3%, the total linear PTHF contents dissolved in the crosslinked samples.

The single chain form factor of the phase-separated linear chains was measured, the results in the intermediate q range tended to suggest that these linear chains are in a partially contracted state as predicted by some theoretical work treating linear chains surrounded by impenetrable obstacles.

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