Communications to the Editor

Molecular Structure of Bimodal Polymer Networks

Introduction. Model polymer networks have been prepared by reacting polymer chains exclusively at their ends. One of the major advantages of this synthetic route is that one can control the chain-length distribution of the resultant network; the chain length within the network must be identical with that before cross-linking. It was observed that for poly(dimethylsiloxane) (PDMS) the networks prepared with a bimodal molecular weight distribution exhibited some unique features compared to those of the unimodal networks.[1] The most noticeable difference is in their ultimate strength before break; the bimodal networks are much stronger or tougher than the unimodal ones. Progress has been made toward an understanding of the molecular origins of this difference in network properties. Stress–strain, stress–birefringence, and stress–temperature measurements were conducted to elucidate the cause of this unusual feature in bimodal networks.[2] However, experiments that can provide a direct characterization of the molecular structure in these networks have not been carried out.

In this short note a set of preliminary results from small-angle neutron-scattering (SANS) measurements of the bimodal polytetrahydrofuran (PTHF) network will be presented. The question to be addressed is whether the short and the long chains are connected randomly in a bimodal network. A random disposition of the long and the short chains within an average network is the obvious choice and is also assumed, at least implicitly, in all previous work. However, in an earlier study of epoxies, SANS results indicated that the short and the long chains were segregated.[3] The definition of segregation needs to be clarified; it does not necessarily imply the existence of long chains and short chains as in the case of segregated block copolymers. Such segregation will be denoted as phase segregation. The other segregation, which will be emphasized in this work, is defined as follows; the makeup of the chemical neighbors of a short chain (or a long one) is not statistically random. In an earlier work, the chemical neighbors of a short chain were found to be long chains and vice versa.[3] Such a segregation will be denoted as molecular segregation. The linear chain analogue of a molecular segregated network is a block copolymer; the short chain (S) and long chain (L) after cross-linking form $(S–L)_n$ or other blocklike structures with a certain degree of regularity.

Materials. For all the SANS specimens, every short chain is deuterated while every long one is hydrogenated. The synthesis of the diallyl-terminated PTHF with narrow molecular weight distribution was carried out according to the method of Smith and Hubin.[4] The number-average molecular weights by chemical titration of the prepolymers used in this work are given in Table I. Two pairs of prepolymers were used and are denoted by the subscripts 1 and 2. The polydispersity of these prepolymers is in the range of 1.1–1.3. The details of the synthesis can be found elsewhere.[5]

Pentaerithritol tetrakis(3-mercaptopropionate) was used as the cross-linking agent, and a stoichiometric amount of it was used for all the samples. The free-radical reaction was initiated with benzopinacole, which is essentially stable until heated. Accelerated activation of cross-linking occurs at temperatures of 80 °C and above.

Table I
Molecular Weight of PTHF Prepolymers

	M_n
L_1	8286
S_1	995
L_2	10034
S_2	1018

Table II
Specifications of SANS Samples

designatn	prepolymers	initiator concn, % wt	molar ratio L:S
A	L_1, S_1	0.19	1:1
B	L_1, S_1	0.14	1:1
C	L_2, S_2	0.6	3:7

Samples A and B were prepared using prepolymer pair 1; one contained 0.19% wt initiator, and the other contained 0.16% wt. For both sets of the samples the molar ratio of the long to short chain was kept at 1:1. Sample C was prepared with prepolymer pair 2 at a molar ratio of long to short chains of 3:7. The initiator concentration used was 1.04% wt. The specifications of the samples are given in Table II.

SANS Measurements. For each of the three sets of samples, SANS measurements were conducted on the uncured, the completely cured, and a few intermediately cured samples. The SANS facility in the Reactor Division of the National Institute of Standards and Technology was used. The sample temperature was kept at 50 °C, a few degrees above the melting point of PTHF, throughout the SANS measurements. The wavelength of the incident neutrons was set at 12 Å, and the q range covered was from 0.005 to 0.08 $Å^{-1}$. After the incoherent component and the empty cell background were subtracted, the scattered neutron intensity was reduced to its absolute scale with a silica gel sample as a secondary scattering standard.

Results and Discussion. The SANS results of sample set A are given in parts A and B of Figure 1. For the uncured sample (Figure 1A), the zero limit of $I(q)$ is estimated to be 0.7 cm^{-1}, which is very close to the theoretical value of 0.74 cm^{-1} for the prepolymer pair assuming ideal mixing and a density of 1.0. This result strongly suggests that the mixing of the long and the short chains in the uncured state approaches that of an ideal solution.

If curing or cross-linking does not induce either molecular or phase segregation between the hydrogenated long chains and the deuterated short chains, the scattering intensity will stay unchanged. This point was illustrated by Wu and Gilmer[6] for the case of random block copolymers. The molecular weight measured by SANS or other scattering methods equals that of the individual prepolymer instead of that of the whole chain. However, as illustrated in the curve labeled as partially cured 1 in Figure 1, a dramatic increase in intensity occurred in the small q range as cure proceeded. This provides unequivocal evidence for segregation. Throughout this work these partially cured samples are labeled as p.cured 1, 2, or 3 and so on. The degree of cure increases with the numerical index. The sample, labeled as p.cured 1, was cured at 85 °C for 3.17 h. The cure times for p.cured 2 and the cured 1 were 31.4 and 67.2 h, respectively. Since the intensity of this sample goes off the scale of Figure 1A, the entire curve is presented in Figure 1B.

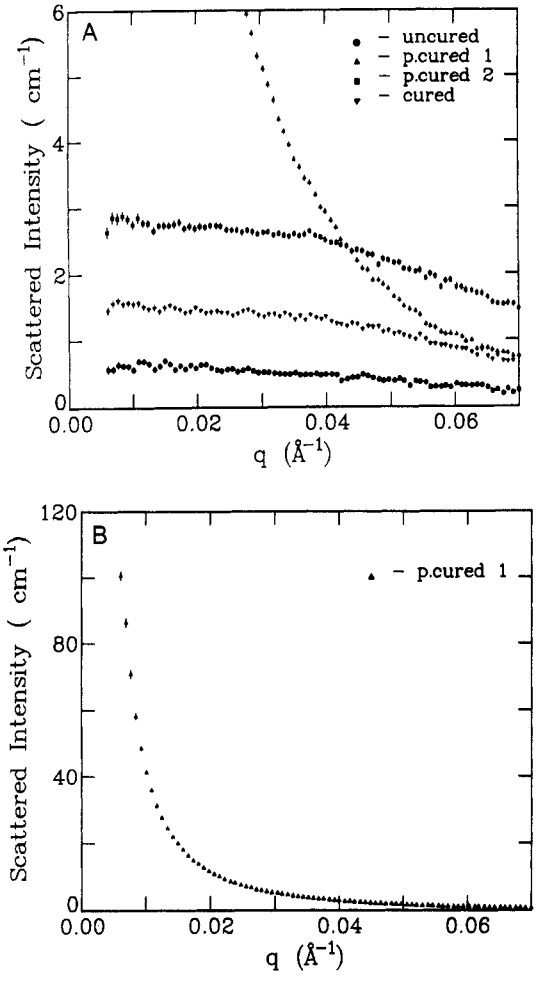

Figure 1. (A) SANS results of sample A at four different stages of cure. The one with a maximum increase in intensity is chosen and labeled as p.cured 1. The curve labeled as p.cured 2 has a higher degree of cure than p.cured 1. (B) Full SANS curve of p.cured 1 of Figure 1A.

From the SANS result of p.cured 1 of Figure 1A alone one cannot yet determine whether the type of segregation is of the phase type or the molecular one. As the cure proceeds to its completion, the scattering intensity, especially in the low q region, exhibits a substantial decrease compared to the partially cured samples. The reasons for this pronounced dropoff in intensity are unknown at this time and will require further investigation.

In addition, a shoulder appears at a q of about 0.04 Å^{-1} in the scattering intensity for the p.cured 2 and the fully cured samples (Figure 1A). This q value corresponds in real space to 25 Å, a reasonable size for the long-chain PTHF used in this work. This shoulder resembles those observed for regular block copolymers. The intensity at the shoulder is only a few times greater than that of the uncured sample in the same q region. This tends to suggest that the segregation is of the molecular type instead of the phase type. Otherwise the peak intensity would be greater than that for a single chain by a few orders of magnitude.

A similar trend in the scattered intensity was also observed in samples B and C. The only difference between sample A and B is the amount of initiator. As listed in Table II, sample B was cured with 27% less initiator than sample A. The SANS results of Figure 2, though, exhibit the same trend as described in the foregoing section for sample A but reveal less segregation during the course

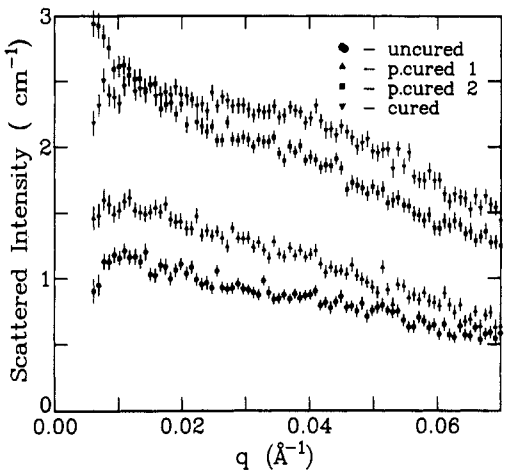

Figure 2. SANS results of sample B at four different stages of cure. The one with a maximum increase in intensity is chosen and labeled as p.cured 1. The curve labeled as p.cured 2 has a higher degree of cure than p.cured 1.

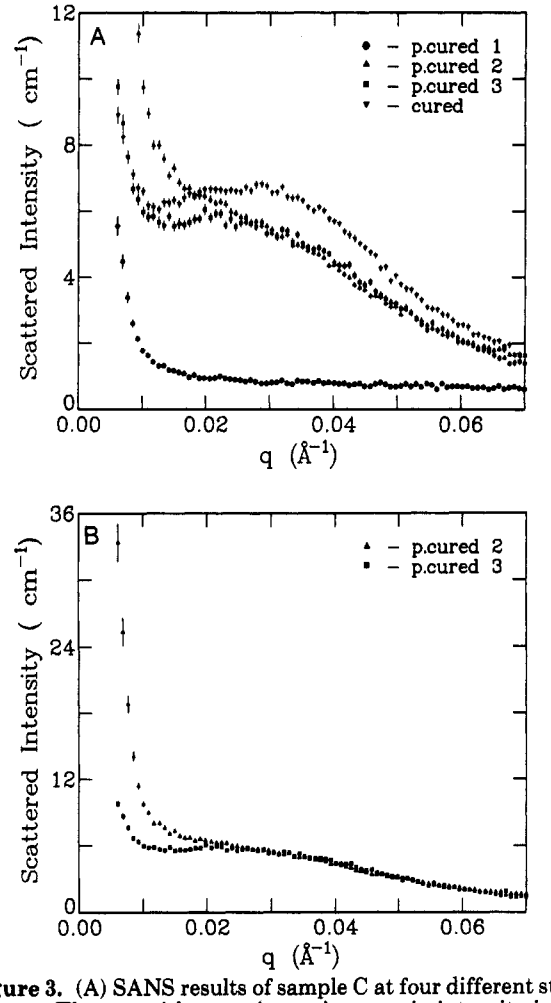

Figure 3. (A) SANS results of sample C at four different stages of cure. The one with a maximum increase in intensity is chosen and labeled as p.cured 2. The curve labeled as p.cured 1 has a lower degree of cure than p.cured 2 and so on. (B) Full SANS curves of p.cured 2 and p.cured 3 of Figure 3A.

of curing. This is apparent by comparing the amounts of increase in the scattered intensity between samples A and B; less of an increase is observed in sample B than in sample A. SANS measurements were conducted on a large number of partially cured samples A and B of different cure times. The scattering intensity first increased

with the cure time and then fell off. The ones at the maximum intensity increase were selected and presented as p.cured 1 on Figure 1A and Figure 2. The above observation tends to suggest that the extent of segregation depends on the initiator content.

The SANS results for sample C, which contains the most initiator among the three samples studied in this work, also reveal an extensive intensity increase in the low q region during the early stage of cure, followed by a decrease in the later stage (parts A and B of Figure 3). In the fully cured sample a rather pronounced maximum is visible. For this set of samples, the SANS result of the uncured sample is absent because the initiator was added to the "uncured" sample; during the course of SANS measurement the temperature was maintained at 50 °C, which resulted in partial curing. (For the other two sets of samples, no initiator was added to the uncured samples.)

At the present time we cannot rationalize all the findings, and more work is apparently needed. Nevertheless, the SANS results covered in this note strongly suggest that cross-linking can induce segregation in bimodal networks. This result is consistent with earlier findings for the epoxy–amine system. In light of this new discovery, some of the earlier observations made on bimodal networks need to be reexamined.

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References and Notes

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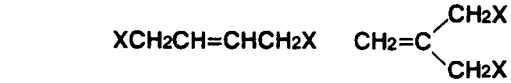
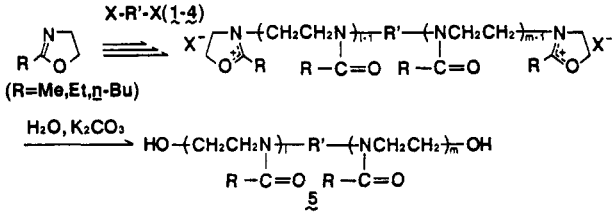
Novel Bifunctional Initiator for Polymerization of 2-Oxazolines via Fast Initiation

Electrophilic (cationic) ring-opening polymerization of cyclic imino ethers produces linear poly(*N*-acylalkylenimines), which become hydrophilic or hydrophobic depending on the nature of acyl group.[1] The polymerization is of highly living nature in using methyl iodide, methyl *p*-toluenesulfonate, and benzyl bromide as a monofunctional initiator, where the initiation rate is very close to or larger than that of propagation.[2] On the other hand, a bifunctional initiator is very important to prepare block copolymers[3] and telechelics.[4] Few examples of such initiators have been reported. α,ω-Dodecamethylene bis(*p*-toluenesulfonate) was first used as a bifunctional initiator for the polymerization of 2-oxazoline.[5] With the use of an alkylene bis(*p*-toluenesulfonate), the molecular weight distribution of the polymer was broad, which implies that the initiation rate was smaller than that of the propagation.[6] However, by using bis(oxazolinium salts) such as 3,3′-ethylene bis(2-oxazolinium trifluoromethanesulfonate)[7] and *N*,*N*′-dimethyl-2,2′-tetramethylene bis(oxazolinium tosylate)[3] as a bifunctional initiator, monodisperse poly(2-oxazolines) were obtained, indicating the relatively fast initiation with respect to the propagation. These salt-type initiators, however, are very elaborative to prepare and inconvenient to handle due to the easily hydrolyzable property. The present paper discloses a novel bifunctional initiator having an allylic dihalide structure **1**–**4** for the polymerization of 2-oxazolines giving rise to a "fast initiation system" of living nature.



1: X=Br **3**: X=I
2: X=Cl **4**: X=Cl

1,4-Dibromo-2-butene (trans) (**1**) and 3-iodo-2-(iodomethyl)-1-propene (**3**) have been used for the first time in this study as a bifunctional initiator for the polymerization of 2-alkyl-2-oxazolines (ROZOs). Initiator **1** is commercially available, and **3** is readily obtained from a commercially available chloro analogue, **4**. Telechelic poly(2-oxazolines) having a hydroxyl group at both ends, **5**, were synthesized by the polymerization of ROZO using



5

these initiators followed by hydrolysis of a terminal oxazolinium group as previously reported.[4] The structure of **5** was confirmed by ^{1}H NMR and IR spectroscopy (Table I). In most cases the yield of polymer **5** was quantitative. The degree of polymerization (DP) of **5** determined by vapor pressure osmometry (VPO) is always very close to the monomer/initiator feed ratio. The M_w/M_n value obtained by gel permeation chromatography (GPC) is relatively small. These results are explained by the rapid initiation followed by the subsequent relatively slow propagation. With use of 1,4-dibromobutane (**6**) as a bifunctional initiator, the DP of **5** was larger than the feed ratio and the M_w/M_n value was large, indicating the slow rate of initiation compared with that of propagation.

1,4-Diiodo-2-butene is not stable enough to be isolated at room temperature. Therefore, sodium iodide was added to the mixture of 1,4-dichloro-2-butene (**2**) (trans:cis = 3:2) and 2-methyl-2-oxazoline (MeOZO) under stirring at 0 °C for 2 h to give an iodide counteranion in situ during the polymerization. The polymer yield was high, and the DP of the polymer was close to the feed ratio (Table II). The M_w/M_n value obtained by GPC is small (1.15). These results can be taken to support that the polymerization is of fast initiation and of slow propagation. Similarly, the polymerization of MeOZO was carried out using 3-chloro-2-(chloromethyl)-1-propene (**4**)/sodium iodide as a bifunctional initiator (entry 11). The DP of the polymer obtained was close to the feed ratio, and the molecular weight distribution evaluated by M_w/M_n was very narrow.

In order to evaluate the reaction rate quantitatively, a kinetic study of the polymerization of MeOZO initiated

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