Equilibrium Swelling and Small-Angle Neutron-Scattering Study on End-Linked Poly(tetrahydrofuran) Networks

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ABSTRACT: The structure of end-linked poly(tetrahydrofuran) networks was investigated by equilibrium swelling and small-angle neutron-scattering (SANS) experiments. The end-linked poly(tetrahydrofuran) networks were prepared by a reaction of telechelic poly(tetrahydrofuran) having -C=C group at both ends with a four-functional cross-linking reagent having -SH groups, where the molar ratio, r, defined by [-SH]/[-C=C] was varied. The molar ratio, r, dependence of the polymer volume fraction at the swelling equilibrium showed a maximum for each network prepared from prepolymers having different number-average molecular weights, M_n. The molar ratio giving the maximum, r_m, increased linearly with M_n, which results from a competition between ideal cross-linking formation with the functionality, f, being 4 and defect formation with $f < 4$, such as three- or two-functional cross-linking and end-capping by cross-linker. The SANS profiles from gels at swelling equilibrium were analyzed with a combination of two types of scattering functions, representing static (solid-like) and solution-like fluctuations. A master relationship was found between these structure parameters and the equilibrium volume fraction, ϕ, which was the same as that for the networks prepared at the stoichiometric condition.

Introduction

Preparation of ideal polymer networks, having a monodisperse molecular weight distribution and an equifunctionality of the cross-links in the entire network, has been strongly desired for structural and mechanical investigations of polymer networks.[1] Mark and Sullivan[2] studied the elastic modulus and the degree of swelling at equilibrium for model poly(dimethysiloxane) (PDMS) networks prepared by a reaction of hydroxyl-terminated PDMS with tetrafunctional orthosilicate. Jong and Stein[3] investigated the elastic behavior for model poly(tetrahydrofuran) (PTHF) networks prepared from allyl-terminated PTHF with a tetrafunctional cross-linker by means of constrained junction theory.[4] They reported that the molecular weights between cross-linking points estimated by fitting of the experimental results with the theory were much smaller than the number-average molecular weights of the prepolymer. This was explained with trapped entanglements in the network which contributed to the modulus of elastomer as effective junction points. Judging from these studies, those networks were not "ideal" model networks because they contain many defects in the network structure, i.e., trapped entanglements, loops, dangling chains, etc.

Networks via telechelic prepolymers are usually prepared from a stoichiometric mixture of prepolymer having functional groups at both ends and multifunctional cross-linker. Patel et al., however, synthesized PDMS networks with different cross-linker/prepolymer ratios and investigated swelling behavior.[5] It was found that there is a maximum of polymer volume fraction at swelling equilibrium, and the peak position was not at the stoichiometric ratio. They explained this by unequal reactivity of the reactive sites of a cross-linker due mainly to its steric hindrance.

Presence of cross-links in polymer networks affects not only the rubber elasticity but also their crystallization behavior and structures. In previous studies,[6,7] we discussed isothermal crystallization kinetics of end-linked PTHF networks. As was expected, the crystallization rate was found to be very sensitive to the cross-linking density or the molecular weights between cross-linking points. Soni and Stein studied the cross-linking heterogeneities in PDMS networks by light scattering.[8] Antonietti et al. synthesized micronetworks from α,ω-living poly(styrene) with a tetrafunctional cross-linker at concentrations low enough to obtain no macroscopic gelation and characterized by light scattering and small-angle neutron scattering (SANS).[9] The structure of the end-linked PTHF networks at swelling equilibrium was also investigated by means of SANS.[10] SANS profiles from gels at swelling equilibrium were decomposed to two contributions from static and dynamic fluctuations. It was found that the relationships among the degree of polymerization, N, of prepolymer, the polymer volume fraction at swelling equilibrium, ϕ, and the correlation length, ξ (the characteristic length of the dynamic fluctuations), are in good agreement with the scaling predictions.[11]

In this paper, the structure of end-linked PTHF networks, prepared by a reaction of telechelic PTHF having -C=C group at both ends with a four-functional cross-linking reagent having -SH groups, is investigated by SANS. The molar ratio, r, defined by [-SH]/[-C=C], the dependence of the volume fraction at swelling equilibrium, ϕ, and the structure parameters are reported followed by a discussion about the roles of cross-link on the network heterogeneity.

Experimental Section

Samples. Telechelic PTHFs having an allyl group at both ends were synthesized by living cationic polymerization. The details of the polymerization are described elsewhere.[6,12] The results of characterization for the prepolymers are shown in Table 1. The number-average molecular weight, M_n, was determined by vapor pressure osmometry (VPO; Knauer). The numbers in the sample code for the networks correspond to M_n of prepolymer. The polydispersity index, i.e., the ratio of the weight and number-average molecular weights, M_w/M_n, was evaluated with a Trirotar II GPC instrument (Jasco Co.,

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Table 1. Sample Codes of Networks and Characterization for Prepolymers

	prepolymer		
sample code	M_n ($\times 10^{-3}$)[a]	M_w/M_n[b]	functionality[c]
U025	2.54	1.15	1.85
U044	4.36	1.17	2.02
U052	5.19	1.17	1.94
U079	7.91	1.18	1.94
U102	10.2	1.20	2.09

[a] By VPO. [b] By GPC. [c] By ^{1}H-NMR.

Ltd., Japan). The functionality of the allyl end groups was evaluated with a 300 MHz QE-300 NMR spectrometer (General Electric).

The preparation of the end-linked networks was carried out by a thiol(SH)−ene(C=C) addition reaction.[3,13] It is known for this reaction that the 1:1 adduct of thiol and ene is produced preferentially and no noticeable side reaction occurs if equal molar amounts of two species are present in a reaction bath. The details of the preparation of end-linked PTHF network are as follows: The prepolymer, pentaerythritol tetrakis(3-mercaptopropionate) [$C(CH_2OCO(CH_2)_2SH)_4$] (Aldrich Chemical Co.) (four-functional cross-linking reagent), and benzopinacol (initiator) were mixed in toluene with different molar ratios of two functional groups, r. After stirring, the solution was transferred into a stainless steel mold and cast at 40 °C. The cast film was held at 88 °C for 48 h in order to complete the cross-linking reaction. After preparation of network, sol fraction was extracted by immersing the network in toluene repeatedly. Then the swollen network film was dipped in methanol to shrink. Finally the shrunken network film was dried in a vacuum oven. The gel fraction was estimated by the weight ratio of the dry network films before and after extraction. It should be noted that pentaerythritol tetrakis(3-mercaptopropionate) was used as a cross-linker, although reagents bearing -SH groups are often used for chain-transfer reactions.

Swelling Experiment. Network films, cut to a disk form, were swollen in toluene at room temperature. The variation of the film diameter, d(t), was measured as a function of time, t.

Small-Angle Neutron Scattering. SANS experiments were carried out at the research reactor SANS-U, Institute of Solid State Physics, The University of Tokyo, located at Japan Atomic Energy Research Institute, Tokai, Japan. Cold neutrons, having the wavelength of $\lambda = 7$ Å, were used as the incident beam. Each network sample at swelling equilibrium with deuterated toluene was irradiated by the neutron beam for 30 min, and the scattered intensity was counted with an area detector. The details of the experiment are described elsewhere.[10]

Results and Discussion

Defects in Networks. First of all, it is of significance to discuss the effect of the variation of r on the defect formation of a network. The cross-linking point is formed by the reaction of at least three -SH groups of the cross-linker having four -SH groups with a -C=C group at the ends of the prepolymer as schematically shown in Figure 1. When r is below unity, i.e., case A, -C=C groups of the prepolymer do not react completely because of the lack of -SH groups. Therefore the prepolymer, of which only one end reacts with a cross-linker, becomes a dangling chain in the network. On the other hand, when $r > 1$, i.e., case B, -SH groups are too many in the reaction bath. Therefore, the probability of three-functional cross-linking and chain extension (with $f = 2$) increases. All of these lead to a decrease of the effective density of the network chains contributing rubber elasticity. The sol fraction also increases for $r \ll 1$ and $r \gg 1$ because of increases of

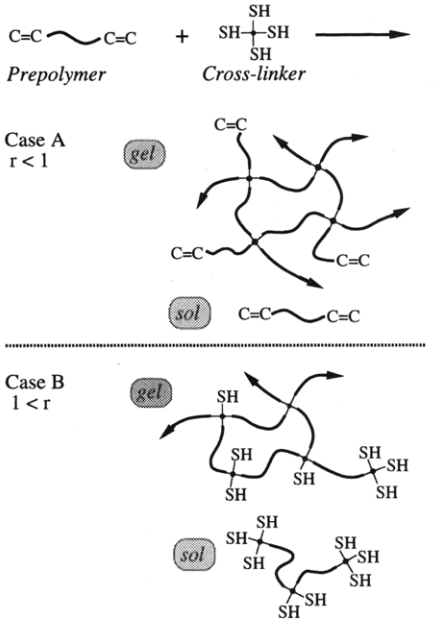

Figure 1. Schematic representation of the cross-linking reaction of the telechelic prepolymers and four-functional cross-linkers. Case A: $r < 1$. Case B: $1 < r$.

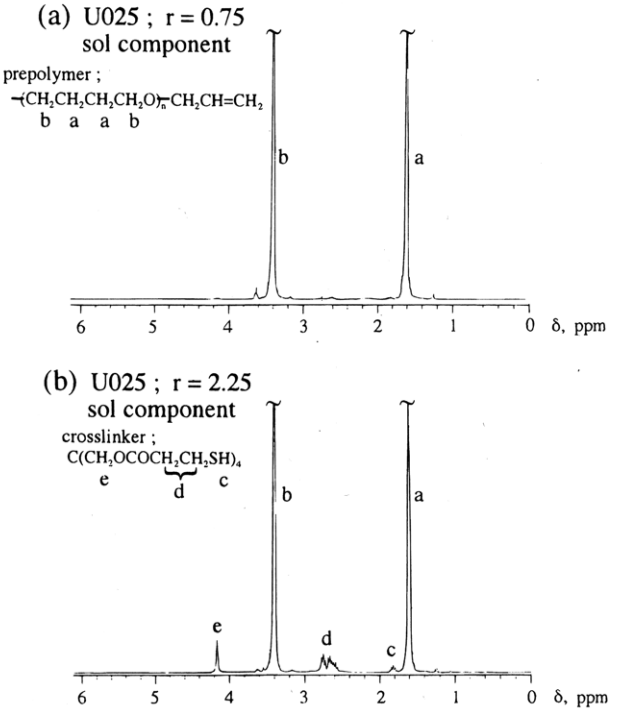

Figure 2. ^{1}H-NMR spectra for the sol components of U025 prepared at (a) $r = 0.75$ and (b) $r = 2.25$. The peak assignment is given in the figure.

the numbers of unreacted prepolymers ($r \ll 1$) and "end-capped" linear polymers ($r \gg 1$).

This speculation is justified with the result of a NMR study. Figure 2 shows the ^{1}H-NMR spectra for the sol component of U025 prepared at (a) $r = 0.75$ and (b) $r = 2.25$. Knowing the spectra for the prepolymer and the cross-linker, we can assign peaks a−e. Peaks a and b correspond to the methylene protons of PTHF, and peaks c−e correspond to the cross-linker. In the case of $r = 0.75$, the sol fraction does not carry noticeable cross-linkers at their chain ends. This indicates that most of the cross-linker was consumed by cross-linking reaction. On the other hand, for $r = 2.25$, it is found

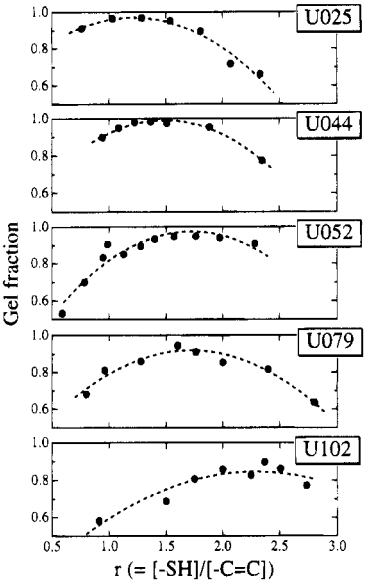

Figure 3. Mercapto group/allyl group ratio, r, dependence of gel fraction.

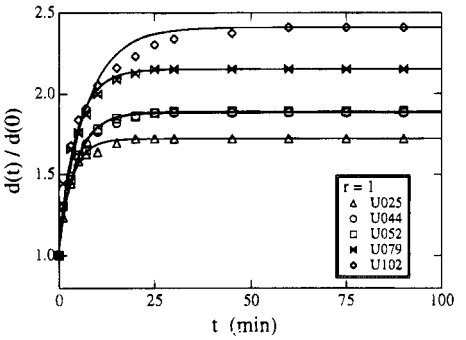

Figure 4. Time evolution of the linear swelling ratio, d(t)/d(0), for the network prepared with the condition of $r = 1$ (stoichiometric network).

from the presence of the peaks c−e that significant amounts of cross-linkers are present in the sol fraction. This indicates that some of the cross-linkers are extracted without cross-linking reaction and the others participate in end-capping reaction of the prepolymer.

Gel Fraction. Figure 3 shows the r dependence of gel fraction for the networks prepared from the prepolymer having different M_ns. The dashed lines in the figure are shown for eye. It is clear that the molar ratio giving the maximum, r_m, exists for each network and r_m shifts to a larger r as M_n increases. These results are consistent with the model in Figure 1.

Swelling. Figure 4 shows the time evolution of the linear swelling ratio, d(t)/d(0), for the networks of $r = 1$ in toluene, where d(0) is the diameter of the network film in a disk form at time $t = 0$. As shown in the figure, an equilibrium swelling is reached within 1 h for all of the samples. The equilibrium swelling ratio, $[d(t)/d(0)]_{eq}$, was estimated from the value at $t = 300$ min and converted to the equilibrium volume fraction, ϕ, with the following equation:

$$\phi = \left[\frac{d(0)}{d(t)}\right]^3_{eq} \tag{1}$$

Another interesting feature of Figure 4 is the swelling kinetics. The time evolution of the reduced gel diameter, d(t)/d(0), was well fitted with the following empirical equation:

$$\frac{d(t) - d(\infty)}{d(0) - d(\infty)} \cong \exp(-t/\tau) \tag{2}$$

where τ is the characteristic relaxation time of swelling. The solid curves in Figure 4 were thus obtained. According to Li and Tanaka,[14] the cooperative diffusion coefficient can be evaluated. However, in this case, the diffusion coefficient is far from a constant since the concentration range (bulk to the equilibrium volume fraction) is too wide to apply the theory. Therefore, further analysis was not conducted at this stage.

Figure 5 shows r dependence of the equilibrium volume fraction of the network, ϕ. As seen in the figure, ϕ varied in the same manner for the gel fraction, i.e., ϕ is a concave function of r and the peak position shifts to larger r as M_n increases. The shifts of peak position, r_m, estimated from ϕ and the gel fraction are shown in Figure 6. It is found that r_m depends rather linearly on M_n of the prepolymer. As discussed in the Introduction, Patel et al.[5] reported that ϕ was dependent on r for networks having the same M_n, and the r_m deviated from the stoichiometric value. They also observed that r_m hardly depended on M_n of the prepolymer. The increase in r_m with M_n, observed here, is explained as follows. It is reasonable to assume that the reaction of the allyl end group of prepolymers with a mercapto group of the cross-linker is determined by the mobility of the prepolymer. If the polymer chains have enough mobility in the bulk due to thermal motion ($T \to \infty$), r_m is independent of M_n and r_m becomes unity. On the other hand, if the mobility of the chain is low enough, one has to add a large amount of cross-linker to compensate the low mobility of the prepolymer and to the conduct the cross-linking reaction. The stoichiometric relation, $r = 1$, means that the concentration of the cross-linker is actually decreased with a power law of M_n^{-1} since the allyl end group concentration decreases with M_n with the same power law. If one keeps the same concentration of allyl groups in the reaction bath, the slope becomes steeper than the observed one of r_m in the figure. Therefore, Figure 6 indicates that the experimental condition employed here is in the middle of the two extremes.

SANS. As described in the pervious paper,[10] a combination of Gauss and Lorentz functions was employed to describe SANS intensity functions, which were originally proposed by Geissler and co-workers[15−19] for analysis of small-angle neutron scattering from a swollen network.

$$I(q) = I_G(0)\exp\left(\frac{-\Xi^2 q^2}{3}\right) + \frac{I_L(0)}{1 + \xi^2 q^2} \tag{3}$$

where q is the magnitude of the scattering vector. $I_G(0)$ and Ξ represent the zero-q intensity and the characteristic mean size of the static (frozen) inhomogeneity, respectively. The Gaussian term can be read as a Guinier function of which Ξ is the radius of gyration of the assemblies of monomer-rich domains (domains of "frozen blob"). The second term of the right-hand side of eq 3 represents solution-like (dynamic) concentration fluctuations. The solution-like concentration fluctuations are simply given by a Lorentz (Ornstein−Zernike) type function.[11] $I_L(0)$ and ξ are the zero-q intensity and the correlation length, respectively.

Figure 7 shows a series of SANS intensity profiles for U052 network prepared with different rs. The open

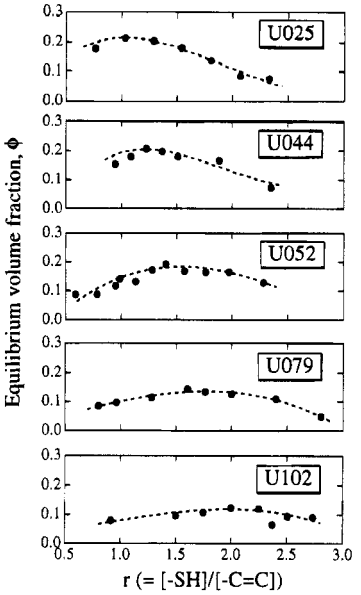

Figure 5. Mercapto group/allyl group ratio, r, dependence of polymer volume fraction, ϕ, at swelling equilibrium.

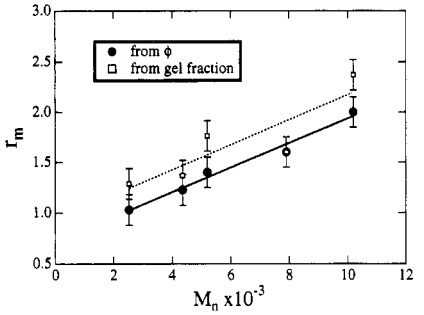

Figure 6. M_n dependence of r_m from polymer volume fraction, ϕ, at swelling equilibrium and gel fraction.

circles indicate the observed scattered intensity, and the dotted and dashed curves denote the Gauss and Lorentz components, respectively. The curve fitting was conducted in the range of $0.0085 \leq q \leq 0.081$ Å^{-1}. It is shown that the scattering intensities vary with ϕ. The structure parameters Ξ, $I_G(0)$, ξ, and $I_L(0)$ are estimated by the curve fitting of eq 3. Figure 8 shows the variations of the static structure parameters, (a) Ξ and (b) $I_G(0)$, against r. The data points are scattered, and no systematic variation with r seems to be present. However, by examining the figures carefully, one finds that each set of the data having the same M_n has a minimum around r_m. A similar behavior is found also for the solution-like structure parameters as shown in Figure 9. Both ξ and $I_L(0)$ are convex functions with r for each set of M_n. Since ξ is related to the mesh size or blob size of the network, the blob size seems to be smallest when $r \approx r_m$. This accords with the model in Figure 1. Since the degree of perfection of the network is highest around $r \approx r_m$, the blob size becomes smallest at $r \approx r_m$.

Scaling Relationship. Since no master relationship was found between the structure parameters, r, and M_n, the data were rearranged with respect to the equilibrium volume fraction, ϕ. Figures 10 and 11 show the ϕ dependencies of structure parameters for static and solution-like fluctuations, respectively. The dashed lines and filled symbols in the figures show the results obtained for the stoichiometirc networks at $r = 1$, e.g., $\Xi \sim \phi^{-0.63}$ and $\xi \sim \phi^{-0.79}$. These indicate that the networks having different M_ns and different internal

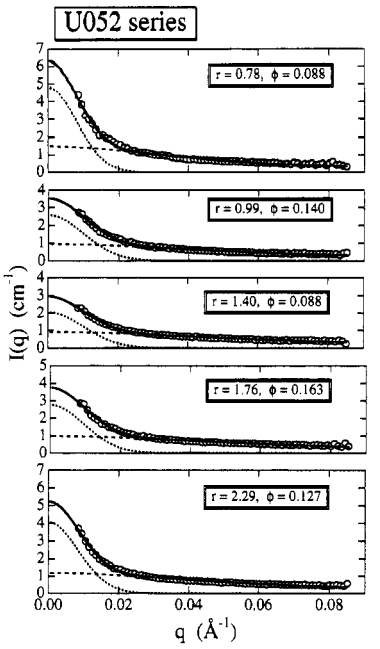

Figure 7. SANS intensity profiles for U052s at swelling equilibrium prepared at different rs. Open circles, dotted curves, and dashed curves denote observed scattered intensity profiles, Gauss component, and Lorentz component, respectively. The solid curves indicate reconstructed intensity profiles.

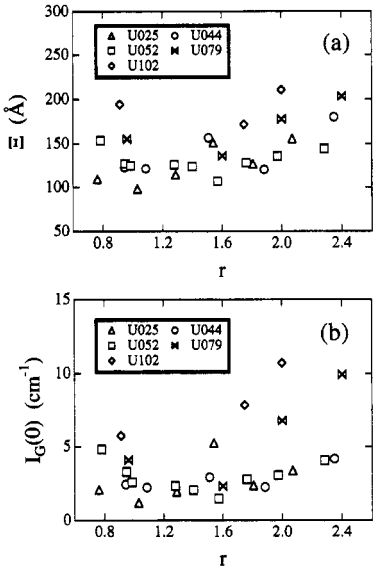

Figure 8. Variation of the static structure parameters, (a) Ξ and (b) $I_G(0)$, with r.

structures (due to different rs) are well described by the same scaling rule as that of the stoichiometric networks by choosing an appropriate parameter, i.e., ϕ. Deviations of the data points for U079 at $r > r_m$ and U102 at $r > 1$ may result from the low efficiency of the cross-linking reaction in the bulk prepolymer.

Concluding Remarks

A series of PTHF networks were synthesized from a mixture of allyl-terminated telechelic poly(tetrahydrofuran) and four-functional cross-linker at different molar ratio, r. The gel fraction and the polymer volume fraction, ϕ, at swelling equilibrium of the networks depend strongly on r and M_n of prepolymer. The r dependencies of the gel fraction and ϕ have the maximum value at $r_m \geq 1$, and r_m linearly increased with M_n. These

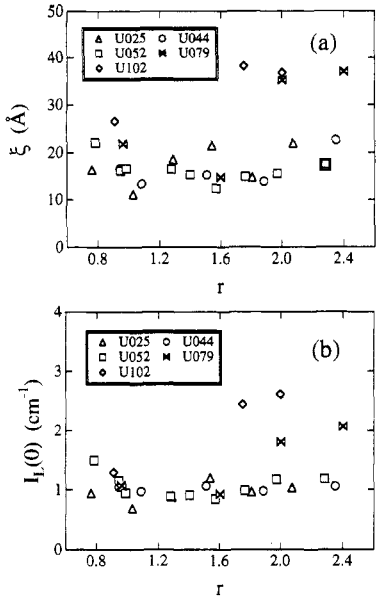

Figure 9. Variation of the solution-like structure parameters, (a) ξ and (b) $I_L(0)$, with r.

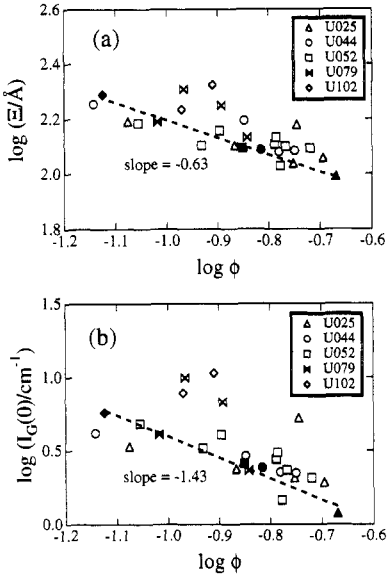

Figure 10. Master relationship showing the ϕ dependencies of the static structure parameters, (a) Ξ and (b) $I_G(0)$. The dashed line and filled symbols indicate the stoichiometric network ($r = 1$).

facts result from the competition between the extent of cross-linking reaction and the incomplete network formation, such as three-functional cross-linking points, chain extension, and/or end capping by cross-linker. The structure parameters, i.e., the size of the frozen domain, Ξ, and its population, $I_G(0)$, as well as the correlation length, ξ, and its intensity, $I_L(0)$, were estimated by SANS. Both the static and solution-like structure parameters are convex functions of r for all the samples having different M_ns. However, a master relationship was found between the structure parameters and ϕ, which is the same as that for the networks prepared at the stoichiometric condition.

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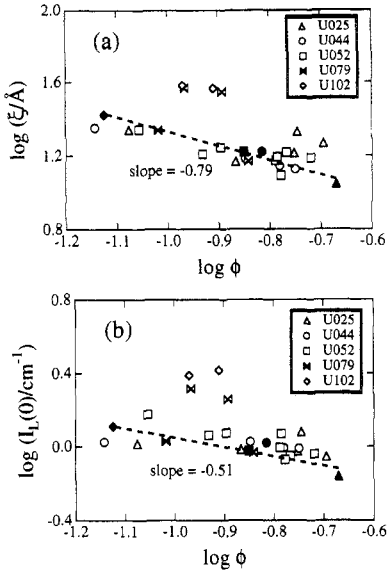

Figure 11. Master relationship showing the ϕ dependencies of the solution-like structure parameters, (a) ξ and (b) $I_L(0)$. The dashed line and filled symbols indicate the stoichiometric network ($r = 1$).

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