Nitroxide-Controlled Free-Radical Copolymerization of Vinyl and Divinyl Monomers. 2. Gelation

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ABSTRACT: Some important features of the gel prepared by the nitroxide-mediated free-radical copolymerization of styrene with a small amount of 4,4′-divinylbiphenyl were studied. Owing to the "living" character of this system, the cross-linking reaction in this system proceeds highly homogeneously (randomly) without forming any microgels. The gel prepared by this method showed remarkable differences from the one prepared in the conventional system, in regard to the relative fraction and swelling ratio of the gel studied as a function of monomer conversion. It was also found that the critical number density of cross-links at the gel point agreed with the mean-field theoretical value of Flory and Stockmayer (FS) within a factor 2. This value was exceptionally small compared with those previously reported for the conventional free-radical systems, which are typically 1 or 2 orders of magnitude larger than the FS value. These results, along with the previous study on the reactivity of the pendant vinyl of this system (Ide, N.; Fukuda, T. *Macromolecules* **1997**, *30*, 4268), show that the gels prepared by this method are exceptionally homogeneous compared with those prepared by the conventional free-radical method.

Introduction

The free radical copolymerization of vinyl monomer with a small amount of divinyl monomer has been widely used to synthesize branched polymers, polymer networks, and gels. These processes have been studied both experimentally and theoretically for a long time. A number of experimental studies[1−12] have shown that the network formation by copolymerization proceeds in a highly nonideal fashion with a large discrepancy from the mean-field theory of Flory and Stockmayer (FS).[13−15] For example, the critical number of cross-links at the gel point experimentally observed for these copolymerization systems was typically 1 or 2 orders of magnitude larger than predicted by the FS theory. This discrepancy arises mainly from the intramolecular cross-links and cyclization,[16] neglected in the FS theory, which make no contribution to the increase in molecular weight. For example, Ulbrich et al.,[5] who studied the copolymerization of *N*-butylmethacrylamide and methylenebisacrylamide, showed that the fraction of cross-links wasted in cycles was very high at the gel point. For the methyl methacrylate and ethylene glycol dimethacrylate system, Okay et al.[12] showed that approximately 30% of the pendant vinyl groups were consumed by cyclization reactions. These experimental results indicate that the spatial distribution of pendant vinyls (around the polymer radical), and hence that of cross-links in the gel, is highly heterogeneous. Inhomogeneous distributions of cross-links were experimentally observed by several methods.[17−20] For example, in a uniaxially deformed gel, Bastide et al.[18] observed "butterfly patterns", unusual scattering spectra arising from a spatially inhomogeneous deformation, which originates from an inhomogeneous cross-link distribution. For poly(*N*-isopropylacrylamide) gels, Shibayama et al.[19] observed that the scattering intensity from such a gel varies from position to position of the sample due to a nonuniform density distribution.

In part 1 of this series of work,[21] we carried out the free-radical copolymerization of styrene (**1**, Figure 1) with a small amount (≤3 mol %) of 4,4′-divinylbiphenyl
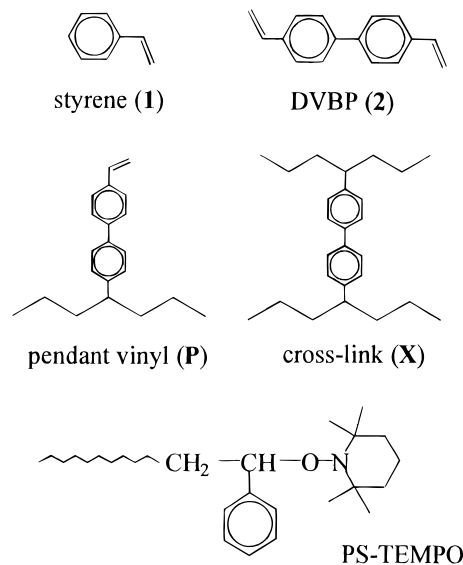

Figure 1. Chemical structures of the monomers (**1** and **2**), the polymerization products (**P** and **X**), and the "initiator" (PS-TEMPO).

(DVBP, **2**) using an oligomeric polystyryl adduct with 2,2,6,6-tetramethylpiperidinyl-1-oxy (PS-TEMPO) as an "initiator". The studied process somewhat resembles the controlled branching (not cross-linking) work by Hawker et al.,[22] who studied the polymerization of a styrenic monomer carrying a TEMPO moiety. Owing to the "living" character of the TEMPO-mediated polymerization of styrenic monomers,[22−28] the copolymerization system was characterized by a slow and simultaneous growth of the primary chains and an essentially constant number of primary chains throughout the course of polymerization. The rate of consumption of the pendant vinyl (**P**) as well as those of monomers **1** and **2** was approximately describable by the simple polymerization theory based on a random distribution of reactants, giving the first well-defined reactivity ratio $r_P = k_{11}/k_{1P}$, where k_{1P}, for example, is the rate constant for

radical **1** to add to **P**. This means that the spatial distribution of the pendant vinyls in this system is much more homogeneous (random) at all stages of polymerization than in the conventional system, if compared at a common level of the (final) concentration and the molecular weight of the primary chains. Therefore, the gel prepared by this method is predicted to be much more homogeneous with less (intrachain) cross-links than those prepared by the conventional free-radical method.

In this work, we have studied some important features of the gel prepared by the nitroxide-mediated method. Topics include the determination of the critical number of cross-links to gel the system and the relative fraction and swelling ratio of the gel as a function of monomer conversion. The results will be discussed in comparison with the FS theory and the gels produced by the conventional free-radical systems.

Experimental Section

Materials. Commercially obtained styrene, benzoyl peroxide (BPO), and TEMPO (Aldrich, Milwaukee, WI) were purified by the standard methods described elsewhere.[25] 4,4′-Divinylbiphenyl and an oligomeric polystyryl adduct with TEMPO (PS-TEMPO) were synthesized as described previously.[4,21] The M_n and M_w/M_n ratio of the PS-TEMPO adduct were 910 and 1.15, respectively, where M_n and M_w are the number- and weight-average molecular weights, respectively. The reason we used the oligomeric PS-TEMPO adduct rather than low-mass alkoxyamines, such as those introduced and/or used by Hawker,[29] Priddy et al.,[30] and others,[25a,31] is simply because a sufficient amount of the oligomeric adduct was in stock and readily available in our laboratory. The low-mass adducts would give essentially the same results as the oligomeric one, as in fact has been shown for the rate of homopolymerization of styrene.[26a]

Copolymerization. Known amounts of the initiator adduct (PS-TEMPO) and DVBP were dissolved in styrene. The mixture, which was charged in a glass tube, degassed with several freeze−pump−thaw cycles, and sealed off under vacuum or argon, was heated at 125 °C for a prescribed time, allowing copolymerization to proceed. The polymer, used in the ultraviolet spectroscopic (UV) analysis (see below), was purified by reprecipitation with a chloroform (solvent)/methanol (nonsolvent) system and thoroughly dried prior to use. This procedure was followed up to a conversion just below the gel point of each mixture.

For reference, conventional copolymerization runs were carried out at 60 °C with BPO as an initiator instead of the PS-TEMPO adduct. The amount of BPO to be used was so determined to make the M_n similar to that of the TEMPO-mediated system at the gel point.

Measurements. The concentrations of pendant vinyls (**P**) and cross-links (**X**) in the copolymer were determined by UV spectroscopy using the model compounds of **P** and **X**, respectively, as detailed previously.[21]

The conversion, C_1, of monomer **1** in the pregel stage was determined by gel permeation chromatography (GPC) and/or gas chromatography (GC). The C_1 in the post-gel stage was determined by weighing the gel before and after removing the residual monomer under vacuum.

The gel point was determined by the tube-inverting method:[32−34] the sample tube with a diameter of 6 mm was placed upside down in a reaction bath. If the reaction mixture did not flow, it was defined as a gel, while otherwise, it was defined as a sol. Some solutions were also studied by dynamic rheometry (Rheometrics, dynamic stress-controlled rheometer, SR-200), where the gel point was defined as the one at which the loss tangent became independent of frequency.[35] The gel points determined by these two methods were generally in good agreement with each other.
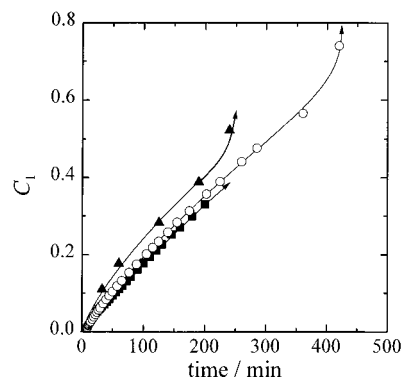

Figure 2. Conversion C_1 vs time curves for the "living" (co)polymerization ([PS-TEMPO] = 34 mmol L^{-1}, 125 °C). Initial feed mole composition of the divinyl monomer, f_2^o: (■) 0, (○) 0.009, (▲) 0.015.

Gel fraction was determined gravimetrically. After a prescribed reaction time, the unreacted monomer was removed by evacuation or precipitation into methanol, and the polymer was thoroughly dried. Then a weighed amount of the polymer was immersed in an excess of toluene, and the solvent was replaced every other day over a period of at least 1 week until no more extract could be detected. Gel fraction, w_g, was determined by weighing the dried polymer after the extraction.

The swelling experiment was carried out by immersing a weighed amount of the purified network in toluene at 25 °C for at least 1 week to reach equilibrium swelling. The swollen network was then weighed to determine the swelling ratio.

The GPC measurements were made on a high-performance liquid chromatograph HLC-802UR (Tosoh, Tokyo, Japan) with tetrahydrofuran as eluent (40 °C). The GC analysis was made on a GC-8A model installed with a PEG6000 column (Shimadzu, Kyoto, Japan).

The UV analysis was done with a Shimadzu UV2200A model by using a quartz cell with an optical path length of 1 cm. Spectroscopic grade 1,4-dioxane (Dotite Spectrosol) was used as a solvent, and the measurements were made at polymer concentrations ranging from 0.5×10^{-3} to 1.0×10^{-3} wt %.

Results and Discussion

The Critical Cross-Link Density of Gelation. It has been established that the rate of TEMPO-mediated styrene polymerization is independent of the adduct concentration:[25−28] for a given conversion, C_1, the length of the primary polymer is inversely proportional to the adduct concentration. This relation was confirmed also in this copolymerization system with various concentration ratios of PS-TEMPO to monomer **1** (1/165 to 1/920). Figure 2 shows the conversion vs time curves for the copolymerization with differing values of f_2^o, where f_2^o is the initial divinyl mole fraction in the feed:

$$f_2^o = N_2^o/(N_1^o + N_2^o) \tag{1}$$

with N_i being the mole concentration of monomer i (=1 or 2), and the superscript "o" denoting the initial state. As the figure shows, the time−conversion curves are somewhat different for different f_2^o: the rate of polymerization, R_p, increases with increasing f_2^o, and this trend is clearer in later stages of polymerization. Since the absolute value of f_2^o is very small in all studied cases, the observed f_2^o dependence of R_p may be ascribed to the dependence of the termination rate constant, k_t, on f_2^o,[26,28] rather than to other causes. As f_2^o increases, the growing (living) chains become branched at an earlier stage of polymerization, which will result in a
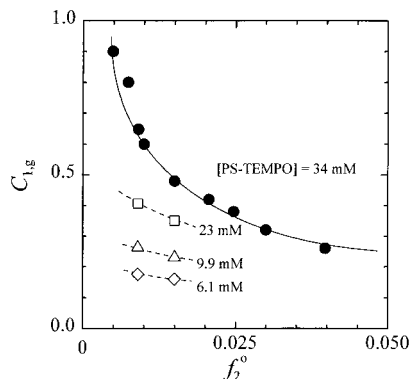
Figure 3. Plot of the critical conversions $C_{1,g}$ of **1** at the gel point vs f_2^o for the "living" copolymerization at 125 °C ([PS-TEMPO] = 34, 23, 9.9, and 6.1 mmol L^{-1} from the top.)

smaller k_t for diffusional and/or steric reason(s). Clearly, the pronounced increase of R_p near the gel point can be attributed to the restricted diffusional motions of highly branched chains, the so-called "gel effect", which was hardly observed in the linear (divinyl-free) system.[26,28]

The critical conversions of **1** at the gel point, $C_{1,g}$, are plotted in Figure 3 against f_2^o. When f_2^o was increased with a fixed adduct concentration, gelation was observed to occur at a smaller conversion (shorter primary chains). On the other hand, when the adduct concentration was increased with a fixed value of f_2^o, the mixture gelled at a larger conversion.

The FS theory gives a prediction for the number of cross-links at the gel point: for the cross-linking of a prepolymer (vulcanization or four-functional random branching), it reads

$$(X_{T,g}/N_o)(M_{w,o}/M_{n,o}) = {}^1/_2 \qquad (2)$$

where N_o and X_T are the concentrations of prepolymer and cross-links, respectively, and the subscripts "o" and "g" denote the prepolymer and the gel point, respectively. This equation means that the critical number of cross-links per prepolymer with the polydispersity effect taken into account is $^1/_2$. It can be rewritten as

$$X_{T,g}/N_2^o = {}^1/_2(N_o/N_2^o)(M_{w,o}/M_{n,o})^{-1} \qquad (3)$$

where N_2^o is the concentration of **2** in the initial feed, as defined before. Thus, the plot of the reduced number of cross-links $X_{T,g}/N_2^o$ against $(N_o/N_2^o)(M_{w,o}/M_{n,o})^{-1}$ should be a linear line with a slope $^1/_2$ passing through the origin. This plot for the "living" system is given in Figure 4 ($M_{w,o}/M_{n,o}$ was set, in all cases, equal to 1.2, the value determined for a divinyl-free system). All data points are represented by a single straight line with a slope of about 1.0. This means that under all studied conditions, gelation occurs when the weight-average number of cross-links per prepolymer reaches about 1.0. This value is only about twice as large as the FS value. It is exceptionally small compared with those previously reported for conventional systems, which are typically 1 or 2 orders of magnitude larger than the FS value.[13–15,21] A difference of a factor of about 2 between the theory and experiment is believed to be ascribed mostly to the failure of the theory to take account of loop formation, rather than to the failure of random statistics (nonuniform distribution of reactants). The previous study[21] has shown that the copolymerization in this "living" system proceeds nearly in a random fashion throughout the
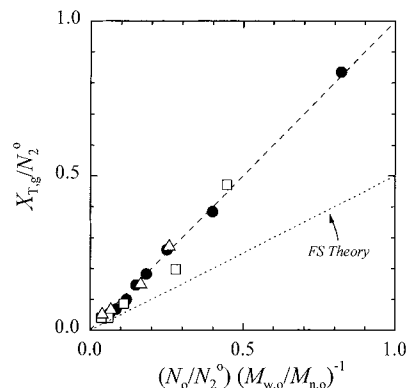

Figure 4. Plot of $X_{T,g}/N_2^o$ vs $(N_o/N_2^o)(M_{w,o}/M_{n,o})^{-1}$ for the data given in Figure 3. The dotted line is theoretical (FS theory) with a slope of $^1/_2$ passing through the origin.
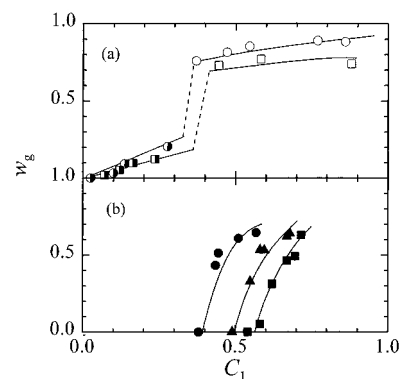

Figure 5. Plot of gel fraction w_g vs C_1 for (a) the conventional and (b) the "living" systems. f_2^o: (○, ●) 0.01, (▲) 0.016, (□, ■) 0.02; (◖ and ◨: micro gels).

Table 1. Feed Compositions and Characteristics of Prepolymers

f_2^o	[PS-TEMPO]/[N_1^o]	$C_{1,g}$	$M_{n,o}$ at $C_{1,g}$	$M_{w,o}/M_{n,o}$ at $C_{1,g}$
		"Living"		
0.010	1/200	0.55	~11 000	
0.016	1/170	0.5	~8 500	~1.2
0.020	1/200	0.4	~8 000	
		Conventional		
0.010	–	0.4	~12 000	
0.020	–	0.35	~10 000	~1.8

course of polymerization. In addition, the polymer concentrations at the gel point may be high enough ($C_{1,g} \approx 0.5$) for the mean-field approach to be valid.

Properties of Gels. Table 1 summarizes values of $C_{1,g}$ and the number-average molecular weight, $M_{n,o}$, and the polydispersity index, $M_{w,o}/M_{n,o}$, of the prepolymer at the gel point. Some similar data for the conventional system are also given in the same table.

Figure 5 shows the plot of gel fraction, w_g, against $C_{1,g}$. In the conventional system, insoluble components (microgels) were detectable even at a *very early* stage of copolymerization ($C_1 < 0.05$). We had not expected this, since, insofar as we were aware, such a result had rarely been reported previously.[10,12] At the gel point, the w_g of the conventional system increased rather abruptly and remained nearly constant up to $C_1 \approx 1.0$. On the other hand, in the "living" system, w_g was perfectly zero up to concentrations just below $C_{1,g}$; the cross-linked polymers produced in the pregel stage were completely soluble, despite their large molecular weights (>10^6 by GPC). Above the gel point, w_g smoothly increased with increasing C_1, and when w_g reached about 0.7, the whole
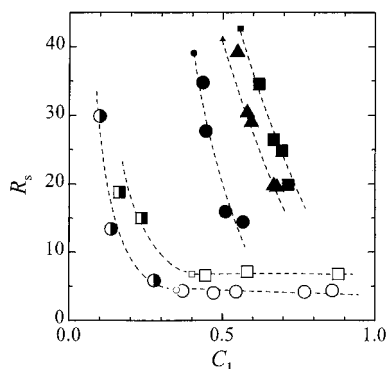
Figure 6. Variation of swelling ratio R_s as a function of C_1 for the conventional (open symbols) and the "living" (filled symbols) systems. See the caption to Figure 5 for symbols. The small symbols indicate the gel point at which the whole solution gelled, showing no flow.

Figure 7. Plot of the average molecular weight M_c between cross-links vs C_1 for the conventional (open symbols) and "living" (filled symbols) systems. See the caption to Figure 5 for symbols. The small symbols indicate the gel point at which the whole solution gelled, showing no flow.

solution changed to an opaque and fragile material that was completely insoluble.

Figure 6 compares the swelling behavior of the purified gels obtained in the two systems. The filled and open symbols refer to the "living" and conventional systems, respectively, and the small symbols indicate the gel point at which the *whole* solution gelled, showing no flow. The data for the conventional system also include those for the microgels produced in the pregel stage. The differences in the swelling behavior between the two systems are very clear. The gels from the "living" system swell better than those from the conventional system. The swelling volume ratio, R_s, in the former system decreases with increasing conversion C_1, hence increasing cross-link density, quite an understandable result. On the other hand, the R_s of the conventional system remains almost constant (in the postgel stage). The difference between the two systems can be more clearly seen by approximately estimating the average molecular weight between cross-links, M_c, according to Flory and Rehner[15,36] (for tetrafunctional cross-linking)

$$M_c = -\rho V_s(\phi_p^{1/3}\phi_0^{2/3} - \phi_p/2)/[\ln(1-\phi_p) + \chi\phi_p^2 + \phi_p] \quad (4)$$

where ρ is the density of the polymer, V_s is the molar volume of solvent (toluene), and ϕ_p is the volume fraction of polymer in a swollen gel ($=R_s - 1$), respectively. ϕ_0 is the so-called memory term, which can be identified with the volume concentration at which the network was generated.[37-39] The polymer–solvent interaction parameter, χ, was assumed to be given by $\chi = 0.431 - 0.311\phi_p - 0.036\phi_p^2$ for the polystyrene/toluene system.[40] Figure 7 shows the plot of M_c vs C_1. The M_c thus estimated for the gels or microgels from the conventional system is not strongly dependent on C_1 and is generally smaller than the M_n of the prepolymer (cf. Table 1), whereas that for the gels from the "living" system is, in the studied range of C_1, much larger than the M_n of the prepolymer, reasonably showing a decreasing trend with increasing C_1.

These differences in w_g and R_s (or M_c) between the two systems clearly suggest differences in the cross-linking processes and the spatial distributions of cross-links arising therefrom. In the conventional system, (dead) polymers of full length are formed from the beginning of the reaction. Since polymers in dilute solution seldom overlap each other, cross-links will be
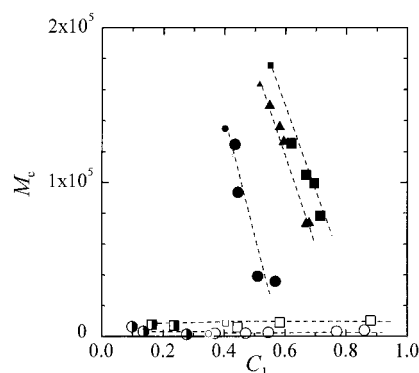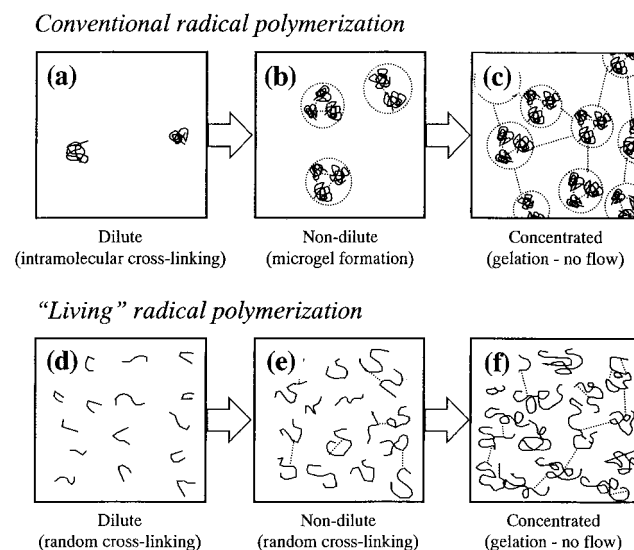
Conventional radical polymerization

"Living" radical polymerization

Figure 8. Schematic presentations of the assumed cross-linking reactions in (a–c) conventional and (d–f) "living" radical polymerization systems.

formed mostly within the same molecule, producing a less expanded (less swollen) chain (Figure 8a). We previously confirmed by light scattering the shrinkage of chains by this cause.[41] As the reaction proceeds, and the number of such chains increases, intermolecular cross-linking will occur more frequently and combine these chains into larger molecules. Once large molecules are formed, they will absorb other chains more effectively than small molecules will, and thus molecules of macroscopic size, i.e., microgels, will be produced even at relatively low conversions (Figure 8b). At a higher (critical) conversion, these microgels will be tied up into a single huge molecule filling the whole space, which will be the gel point observed by the mentioned mechanical methods (Figure 8c). In this picture, the gel from the conventional system is essentially a collection of weakly combined microgels, and accordingly, it is highly heterogeneous, exhibiting swelling behaviors similar to those of microgels themselves, which have a relatively high cross-link density, at all conversions. Hence this picture is consistent with the observed M_c vs C_1 as well as w_g vs C_1 relations. In the "living" system, on the other hand, the concentration of primary chains is high and constant from the beginning of the reaction, so that cross-links will be introduced nearly

randomly throughout the course of polymerization to give a well-defined gel point and a highly homogeneous gel (Figures 8d−f). That the gel from the "living" system is highly homogeneous (compared with that from the conventional system) has been indicated by several experimental facts: first, as the conversion increases, the system reaches a well-defined gel point without forming any microgels; second, this gel point agrees with the FS mean-field theory[13−15] within a factor of 2, and this difference is reasonably ascribed mainly to the failure of the theory to take account of the loop formation that will inevitably occur even in a perfectly random system (see above); third, the previous kinetic analysis[21] shows that the copolymerization process may be approximately described by random statistics; fourth, the parameters w_g, R_s, and M_c qualitatively vary with conversion as expected by the mean-field theory[13−15] (hence as expected for a homogeneous gel), even though quantitative comparison with the theory is difficult to make because of the mentioned difference in the gel point.

Conclusions

The free-radical copolymerization of styrene with a small amount (≤ 3 mol %) of 4,4′-divinylbiphenyl was carried out with an oligomeric PS-TEMPO adduct as an initiator. Owing to the "living" character of this system, the cross-linking reaction proceeds highly homogeneously without forming any microgels. The critical number density of cross-links $X_{T,g}/N_0$ of gelation agrees with the FS theory within a factor of 2. This value is exceptionally small compared with those previously reported for conventional systems, which are typically 1 or 2 orders of magnitude larger than the FS value. Other differences between the two systems in the relative fraction and swelling ratio of the gel as a function of monomer conversion clearly suggest differences in the cross-linking processes and the spatial distribution of cross-links arising therefrom. The gel prepared by the "living" radical method is, thus, much more homogeneous than that prepared by the conventional method. The homogeneity of a gel will be reflected not only by its optical[18,19] and swelling properties but by its mechanical characteristics; for example, the elastic modulus of the homogeneous gel prepared by the nitroxide method should be much larger than that of the conventional one when compared at a common level of average cross-link density and primary-chain length.[42] Other methods of "living" radical polymerization, such as ATRP (atom transfer radical polymerization),[43] would give essentially the same results as the nitroxide method.

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