Nitroxide-Controlled Free-Radical Copolymerization of Vinyl and Divinyl Monomers. Evaluation of Pendant-Vinyl Reactivity

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ABSTRACT: The free-radical copolymerization of styrene (monomer 1) with a small amount ($\leq$3 mol %) of 4,4′-divinylbiphenyl (monomer 2) was carried out at 125 °C with an oligomeric polystyryl adduct with 2,2,6,6-tetramethylpiperidinyl-1-oxy (PS-TEMPO) as an "initiator". Owing to the "living" character of the TEMPO-mediated polymerization of styryl monomers, this system is 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 C_p vs C_1 as well as C_2 vs C_1 curves of this system were approximately describable by the simple polymerization theory based on a random distribution of reactants, giving $r_1 = 0.38$ and $r_p = 1.0 \pm 0.1$. Here C_1, C_2, and C_p are the conversions of monomer **1**, monomer **2**, and pendant vinyl, respectively, and $r_1 = k_{11}/k_{12}$ and $r_p = k_{11}/k_{1p}$, with k_{1p}, for example, being the rate constant for radical 1 to add to pendant vinyl. This system thus makes a sharp contrast to conventional free-radical systems, where the determination of r_p is extremely difficult due to the intramolecular cyclization that can occur to a serious degree even at $C_1 = 0$.

Introduction

The free-radical copolymerization of a vinyl monomer with a small amount of a divinyl monomer offers one of the simplest routes to the preparation of polymer networks and gels. However, a number of experimental studies[1−12] commonly suggest that the network formation by this method proceeds in a highly nonideal fashion, showing a large discrepancy from the classical theories of Flory and Stockmayer (FS).[13−16] A major cause for the discrepancy is believed to be the formation of cycles or intramolecular cross-links.[17] For example, Mrkvicková and Kratochvíl,[10] who studied the copolymerization of methyl methacrylate with a dimethacrylate monomer, observed that the majority of pendant vinyls are consumed by an intramolecular reaction, causing little increase in the molecular weight of the system. For styrene systems, Haward et al.[6,7] showed that, even in the limit of zero conversion, tens of percent of the pendant vinyls sparsely introduced in the chain had reacted, hence forming a number of cycles in the primary chain. These observations indicate that the spatial distribution of pendant vinyls (around the polymer radical) is highly heterogeneous. From a viewpoint of kinetic studies, this suggests an extreme difficulty of determining the *intrinsic reactivity* of pendant vinyls, i.e., the reactivity that would be observed for a hypothetical random distribution of the reactants.

An experimental criterion of random distribution would be the independence of the reactivity ratio r_p on conversion and feed monomer ratio (excepting extreme cases such as very high conversions), where

$$r_p = k_{11}/k_{1p} \qquad (1)$$

with k_{11} and k_{1p} being the rate constants of the polymer radical 1 to add to monomer **1** and pendant vinyl **p**, respectively. Since cross-linking is a second-order reaction with respect to polymer (or polymer radical) concentration, no cross-links should be formed in a random system in the limit of zero conversion. The nonzero conversions of pendant vinyls observed in the limit of zero monomer conversion[6,7,12] would therefore lead to the erroneous conclusion that $k_{1p} = \infty$ or $r_p = 0$, if the system is treated as if a random one. This is more or less true at any level of conversion, and there is no a priori rigorous method to correct for the nonrandomness of the distribution. For this reason, the determination of r_p has been considered to be an extremely difficult problem, and many workers have simply introduced the assumption of equal reactivity of monomeric and pendant vinyls without experimental justification. Landin and Macosko[12] have tackled this problem by introducing some simplifying assumptions on cyclization processes and postulating the validity of the FS theory at the critical conversion of gelation. Their results indicated that the pendant vinyl reactivity in the methyl methacrylate/ethylene glycol dimethacrylate system is about half that of the monovinyl reactivity.

In this work, we attempt to evaluate the r_p of the styrene (S)/4,4′-divinylbiphenyl (DVBP) system by a new approach. It is based on the use of 2,2,6,6-tetramethyl-1-(oligo−polystyroxy)piperidine (PS-TEMPO) as an initiator. At high temperatures, this compound *reversibly* dissociates into an oligomeric PS radical and a TEMPO radical.[18] Thus, in the presence of the monomer (S), the PS radical undergoes propagation until deactivated again by a TEMPO radical, forming a new polymer−TEMPO adduct. A number of such activation−deactivation cycles allow all the primary chains to grow slowly at the same mean velocity, producing polymers with a narrow polydispersity.[19] We have examined the kinetic details of the TEMPO-mediated polymerization and copolymerization of styryl monomers and showed that the system may be *approximated,* at least under limited conditions, by a living system with a nearly constant number of polymer chains throughout the course of polymerization[20−24] (see, e.g., Figure 2 in ref 21 for typical experimental results). This method, when applied to the vinyl/divinyl copolymerization, would make a new system that is entirely different from the conventional one: since in the TEMPO-mediated system all (primary) chains grow slowly and simultaneously starting with the oligomeric initiator, the spatial distribution of the pendant vinyls would be much more homogeneous (random) than that in the conventional system at all stages of polymerization, if compared at a

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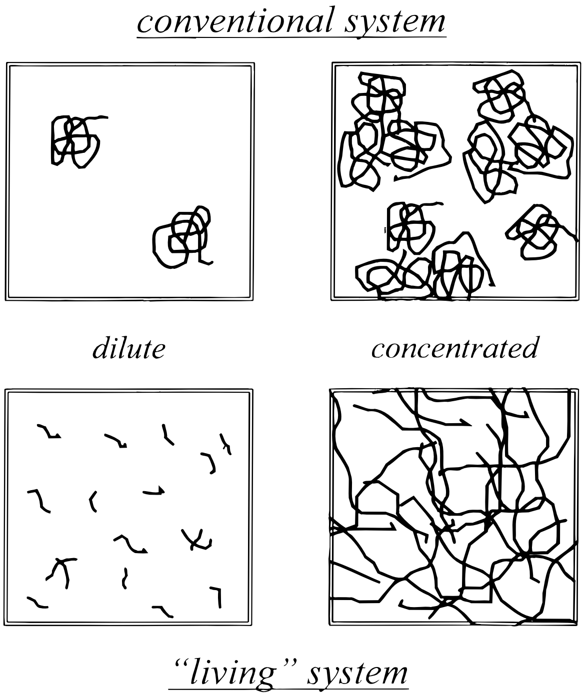

Figure 1. Schematic presentations of the assumed differences between the conventional and living radical polymerization systems.

common level of the (final) molecular weight of the primary chain (Figure 1).[25] With this new system, one can thus expect to evaluate the r_p of the S/DVBP system, if still approximately, without introducing any assumptions about the pendant vinyl distribution or cross-linking processes. We will show below that this system, in fact, meets the above-mentioned criterion of random distribution (constancy of r_p), albeit approximately.

Experimental Section

Materials. Styrene, benzoyl peroxide (BPO), azobis(isobutyronitrile) (AIBN), 4,4′-diisopropylbiphenyl (DPBP), and TEMPO (Aldrich, Milwaukee, WI) were purified by distillation or recrystallization.

4,4′-Divinylbiphenyl (DVBP) was synthesized according to the literature procedure,[29,30] which starts with biphenyl and proceeds via the preparation of 4,4′-bis(chloromethyl)biphenyl and then biphenylyl-4,4′-bis(methyltriphenylphosphonium chloride). We used 1,4-dioxane instead of CCl_4 used in the literature.[29]

4-Ethyl-4′-vinylbiphenyl (EVBP) was synthesized from 4-ethylbiphenyl by the same procedure as for DVBP.

An oligomeric polystyryl adduct with TEMPO (PS-TEMPO) was prepared by heating a styrene solution of BPO (70 mmol L^{-1}) and TEMPO (84 mmol L^{-1}) at 125 °C for about 5 h.[21] After purification, it was found to have an M_n of 910 and a M_w/M_n ratio of 1.15, where M_n and M_w are the number- and weight-average molecular weights, respectively. A chain-extension test[21] suggested that the fraction of the inactive species (molecules without a TEMPO moiety at the chain end) is less than 5%, if there is any.

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

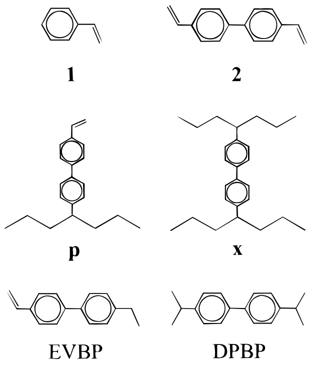

Figure 2. Chemical structures of the monomers (**1** and **2**), the polymerization products (**p** and **x**), and the model compounds for **p** and **x** (EVBP and DPBP) used in the UV analysis.

For reference, conventional copolymerization runs were carried out at 50 °C with AIBN as an initiator instead of the PS-TEMPO adduct. *p*-Methoxyphenol was added to the system as a chain-transfer agent to adjust the molecular weights of the produced polymers so that they are approximately the same as those of the TEMPO-mediated living copolymerization runs at the critical conversions of gelation.

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

The UV analysis[7] was made with a Shimadzu UV2200A model by using a quartz cell with an optical path length of 1 cm. Spectroscopic-grade 1,4-dioxane (Dotite Spectorosol) was used as a solvent, and the measurements were made at concentrations of the sample polymers ranging from 0.5×10^{-3} to 1.0×10^{-3} wt %.

Results and Discussion

Our system involves three kinds of vinyl groups, which are monovinyl (**1**), divinyl (**2**), and pendant vinyl (**p**), as illustrated in Figure 2. Within the framework of the terminal model,[31] we therefore have three kinds of polymer radicals and a total of nine rate constants k_{ij} (i, j = 1, 2, or p) to be distinguished,[12] where k_{ij} is the rate constant for radical i to add to vinyl j. In this work, we are interested in the special case where $M_1 \gg M_2$ (and $M_1 \gg M_p$), with M_j being the mole concentration of vinyl j. In such a case, the kinetic behavior of the system is practically independent of the values of k_{2j} and k_{pj} (j = 1, 2, or p), since the concentrations of radicals 2 and p are much smaller than that of radical 1. For this reason, we may approximately write $k_{i1} = k_{11}$, $k_{i2} = k_{12}$, and $k_{ip} = k_{1p}$ (i = 2 or p), when the rate equations reduce into the following three:

$$\mathrm{d}M_1/\mathrm{d}t = -k_{11}M_1R \tag{2}$$

$$\mathrm{d}M_2/\mathrm{d}t = -k_{12}M_2R \tag{3}$$

$$\mathrm{d}M_p/\mathrm{d}t = (k_{12}M_2 - k_{1p}M_p)R \tag{4}$$

where R is the total radical concentration at time t. These equations can be solved, by appropriately eliminating R from them, to yield

$$M_2/M_2^0 = (M_1/M_1^0)^{1/r_1} \tag{5}$$

$$M_p/M_2^0 = [r_p/(r_p - r_1)][(M_1/M_1^0)^{1/r_p} - (M_1/M_1^0)^{1/r_1}] \tag{6}$$

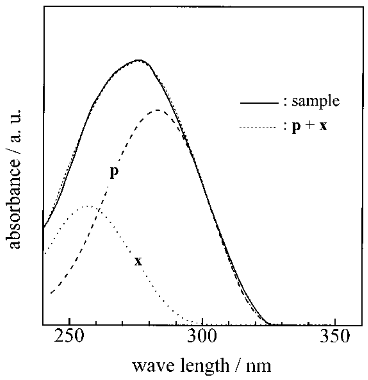

Figure 3. Example of UV spectra.

where

$$r_1 = k_{11}/k_{12} \tag{7}$$

with r_p as defined by eq 1 and the superscript “0” denoting the initial state ($t = 0$).

Equations 5 and 6 give the conversion C_2 of divinyl monomer and the conversion C_p of pendant vinyl as a function of the feed monomer composition f_2^0, the monovinyl conversion C_1, and the reactivity ratios r_1 and r_p, where

$$f_2^0 = M_2^0/(M_1^0 + M_2^0) \tag{8}$$

$$C_1 = 1 - M_1/M_1^0 \tag{9}$$

$$C_2 = 1 - M_2/M_2^0 \tag{10}$$

$$C_p = M_x/(M_p + M_x) \tag{11}$$

In eq 11, M_x is the mole concentration of cross-links, i.e., the divinyl monomers with both of the vinyls reacted:

$$M_x = M_2^0 - M_2 - M_p \tag{12}$$

Thus, the measurements of M_p and M_x at varying values of f_2^0 and C_1 allow us to evaluate r_1 and r_p and test the validity of the theory that is based on the random distribution of the reactants.

The determination of M_p and M_x in the S/DVBP system was made by UV spectroscopy,[7] with EVBP and DPBP used as model compounds for p and x, respectively (cf. Figure 2). Figure 3 gives an example of the spectrum from a copolymer solution, which, by referring to the spectra of the model compounds, can be divided into the two components p and x, as shown in the figure. Knowing the molar absorption coefficients of EVBP and DPBP of 2.77 × 10^4 L mol^{-1} cm^{-1} (at 282.6 nm) and 2.34 × 10^4 L mol^{-1} cm^{-1} (at 257.2 nm), respectively, we thus determined M_p and M_x (and M_2 from eq 12).

Figure 4 shows the plot of $\log(M_2/M_2^0)$ vs $\log(M_1/M_1^0)$ for various values of f_2^0. The concentration of the initiator PS-TEMPO was fixed at 34 mmol L^{-1}. The data points may be represented by a single straight line, whose slope gives $r_1 = 0.38$, according to eq 5. Since DVBP has two vinyl groups, the value of $(2r_1)^{-1} = 1.3$ measures the reactivity of a vinyl group in DVBP relative to that of styrene. This shows that DVBP is somewhat more reactive to PS radical than styrene is.

The value of r_1 obtained here well agrees with the value of 0.39 estimated by Holdaway et al.[7] for the conventional copolymerization of the same monomers in a 15 wt % toluene solution at 95 °C. Fukuda et al.[22] have shown that a styrene–acrylonitrole random copolymer prepared by the nitroxide-controlled living radical method has the same microstructure as the one prepared by the conventional method. These indicate that the reactivity ratio determined in the nitroxyl system may be used in the conventional system and vice versa. This, of course, applies also to the r_p value discussed below.

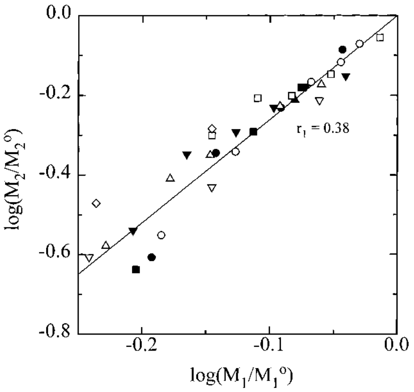

Figure 4. Plot of $\log(M_2/M_2^0)$ vs $\log(M_1/M_1^0)$ for the living radical copolymerization at 125 °C with [PS-TEMPO] = 34 mmol L^{-1}: f_2^0 = 0.020 (■), 0.017 (●), 0.015 (▲), 0.014 (▼), 0.0099 (□), 0.0089 (○), 0.0070 (▽), 0.0050 (△), and 0.0026 (◇). The straight line is theoretical with $r_1 = 0.38$.

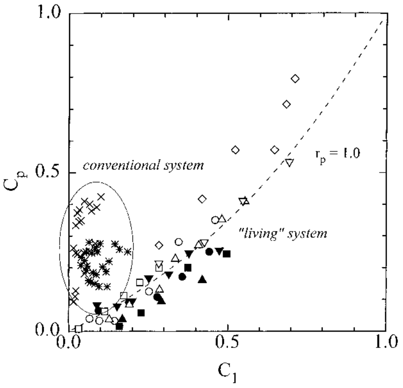

Figure 5. Plot of C_p vs C_1 for the living radical copolymerization at 125 °C with [PS-TEMPO] = 34 mmol L^{-1} and various values of f_2^0 (see the caption to Figure 4 for symbols); the broken curve is theoretical with $r_p = 1.0$ and $r_1 = 0.38$; the M_n of the primary chains may be given approximately by $M_n = 910 + 17000C_1$. The figure includes the experimental data for the conventional systems obtained by Holdaway et al.[7] (×: in 15 vol % toluene solution at 95 °C with f_2^0 = 0.0048–0.030) and by us (*: [AIBN]/[monomer] = 0.015, f_2^0 = 0.0049–0.013; the M_n of the primary chains ranged from about 10 000 to about 19 000 depending on the amounts of the added chain-transfer agent, *p*-methoxyphenol, which ranged from 16 to 30 wt %).

Figure 5 shows the plot of C_p vs C_1. For comparison, the figure includes similar data for the conventional systems obtained by Holdaway et al.[7] (toluene solution at 95 °C) and in this work (see the Experimental Section). As was already suggested, the data of Holdaway et al.[7] give C_p ranging from about 0.2 to about 0.4 at $C_1 = 0$, depending on f_2^0. Our data for the conventional system also indicate a similar range of C_p values at $C_1 = 0$. Since, for small C_1, it holds that

$$C_p = C_1/2r_p \qquad (C_1 \ll 1) \tag{13}$$

the experimental results for the conventional systems suggest that r_p is very small and strongly dependent on C_1. The behavior of the living radical system is entirely different, as Figure 5 shows. Even though experimental points are somewhat scattered, they can be described by the theoretical curve with $r_p = 1.0 \pm 0.1$ (and $r_1 = 0.38$) in the whole ranges of f_2^0 and C_1 examined. Thus, this system meets the above-mentioned criterion of the random distribution of pendant vinyls, though approximately.

The value of r_p^{-1} of about 1.0 obtained here is significantly smaller than the value of 1.3 for $(2r_1)^{-1}$, indicating that the reactivity of the pendant vinyl is lower than that of the free vinyl of the divinyl monomer. This suggests that the polymer chain to which the pendant vinyl is connected reduces the reactivity of the pendant vinyl, perhaps working as a steric barrier.[12] The concentration of polymer segments around a growing radical would be more or less higher than the bulk (mean) concentration at any level of conversion, because of the presence of the chain to which the radical belongs. We have seen that the effect of this local inhomogeneity appears most drastically in the intramolecular cyclization in the conventional system with low conversions. In the living radical system, this effect is largely suppressed by an increased chance of intermolecular reactions relative to that of intramolecular reactions, resulting in the well-defined value of r_p. However, we cannot expect that the estimated r_p value is perfectly free from this local inhomogeneity effect. It is still possible that we are somewhat underestimating r_p. Then the true reactivity r_p^{-1} of the pendant vinyl can be even smaller than 1.0.

Conclusions

The free-radical copolymerization of styrene with a small amount ($\leq$3 mol %) of DVBP was carried out with an oligomeric PS-TEMPO adduct as an initiator. Owing to the living character of this system, the C_p vs C_1 as well as C_2 vs C_1 curves were approximately describable by the simple polymerization theory based on a random distribution of reactants, giving $r_1 = 0.38$ and $r_p = 1.0 \pm 0.1$. This system thus makes a sharp contrast to the conventional systems, in which the determination of r_p is extremely difficult due to the intrachain cyclization that can occur to an often serious degree even at $C_1 = 0$. These results suggest that the gels prepared by this method may be much more homogeneous with less intrachain cross-links than those prepared by the conventional free-radical method. This will be the topic of a forthcoming paper.[32]

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