Notes

Well-Defined Random Copolymers by a "Living" Free-Radical Polymerization Process

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A general method for the random copolymerization of vinyl monomers to give low-polydispersity macromolecules with accurate control over molecular weight and chain ends has long been a goal of synthetic polymer chemists. However, many of the traditional methods for controlling polymeric structure, such as anionic,[1] cationic,[2] or group transfer procedures,[3] are not well suited for the preparation of well-defined random copolymers from disparate vinyl monomers, such as styrenics and acrylates. Also, the demanding reaction conditions of anionic or cationic techniques severely limit the compatibility of many functional groups with these techniques. For these reasons, the synthesis of many random copolymers can only be accomplished under normal free-radical procedures where the ability to control macromolecular structure and molecular weight distribution is lacking. Recently, the concept of "living" free-radical polymerization[4] has attracted considerable interest due to the accurate control over molecular weight,[5] chain ends,[6] and macromolecular architecture[7] afforded by this novel procedure. The main focus of this work, however, has been directed toward the synthesis of polystyrene derivatives, and the application of this technique to the control of random copolymer structure has not been examined in detail with the exception of Georges' reported[8] copolymerization of styrene and butadiene. This is unfortunate, since the living free-radical system, based on TEMPO as a mediating counterradical, occurs by a modified free-radical polymerization process which could permit the preparation of well-defined random copolymers. This paper reports the use of unimolecular initiators, based on 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as a mediating counterradical, and "living" free-radical polymerization procedures for the synthesis of a wide variety of random copolymers with well-defined end groups, controlled molecular weights, and low polydispersities.

Initially, the random copolymerization of styrene with either methyl methacrylate or butyl acrylate under living free-radical conditions was examined for a variety of monomer feed ratios. The polymerizations were performed in the bulk under an inert atmosphere at oil bath temperatures of 125−130 °C for 72 h with the hydroxy derivative **1** as the unimolecular initiator.[7] As can be seen in Table 1, excellent agreement between the observed molecular weights and the theoretical molecular weight of 9500 amu[9] is observed at high styrene ratios, with extremely low polydispersities being obtained. For example, heating a neat mixture of styrene and butyl acrylate (feed ratio 8:2) at 130 °C for 72 h resulted in an 81% yield of the polymer **3**, which was shown to have a molecular weight, M_n, of 9000 and a polydispersity of 1.22 (Scheme 1).[10] The evolution of molecular weight with monomer conversion was examined for three systems: 8:2, 7:3, and 6:4 styrene/butyl acrylate. In each case, an approximately linear relationship was observed. This is similar to the finding of Georges[8] for the homopolymerization of styrene and suggests that these copolymerizations are also proceeding by a living process. For all the copolymers reported in Table 1, proton NMR analysis confirmed that the ratio of repeat units in the polymer **3** was essentially the same as that expected from the feed ratio. As the styrene ratio decreases, for both the methyl methacrylate and *n*-butyl acrylate series, the polydispersity is observed to increase while the difference between the experimental and theoretical molecular weights also increases. However, it should be noted that the control over macromolecular structure is significantly greater than with classical free-radical techniques, with the observed polydispersities for all copolymers with greater than 50% styrene below the theoretical lower limit of 1.50 for a normal free-radical process.[11]

The synthetically nondemanding aspect of living free-radical polymerizations can also be exploited in the preparation of well-defined random copolymers containing reactive functionalities. For example, *p*-(chloromethyl)styrene, which, due to the reactivity of the chloromethyl group, cannot be polymerized by cationic or anionic techniques, undergoes ready copolymerization with styrene under living free-radical polymerization conditions. Heating the unimolecular initiator **1** with 200 equiv of styrene and *p*-(chloromethyl)styrene (9:1 molar ratio) gives the corresponding random copolymer in 88% yield. The copolymer was found to have a number-average molecular weight, M_n, of 19 700 and a polydispersity of 1.21, which compares favorably with the theoretical molecular weight of 21 750.[12] A variety of monomer units, as, for example, acrylonitrile, hydroxyethyl methacrylate, *p*-(hydroxymethyl)styrene, and *N*-vinylpyrrolidone, could also be copolymerized with styrene to give well-defined copolymers.

To determine whether the controlled random copolymers prepared by living free-radical polymerization procedures have the same sequence distribution as macromolecules prepared by classical free-radical techniques, the 300 MHz proton NMR spectra of the styrene/methyl methacrylate copolymers, **3**, were examined in detail at 55 °C in $CDCl_3$. As can be seen in Figure 1, the region from 2.0 to 3.8 ppm, which is due to methoxy group of the methyl methacrylate unit, undergoes dramatic changes as the percentage of styrene is increased from 30 to 80%. These changes in the resonance for the methoxy group are due to variations

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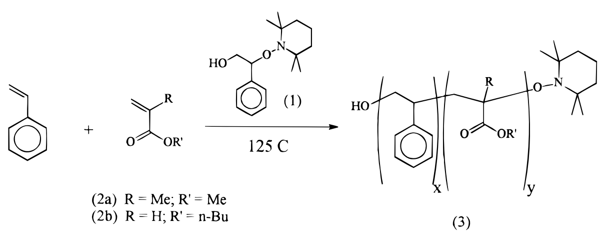
Table 1. Experimentally Determined Molecular Weights (M_n) and Polydispersities (PD) for Random Copolymers of Styrene and either Methyl Methacrylate or *n*-Butyl Acrylate Prepared by "Living" Free-Radical Procedures

	methyl methacrylate		*n*-butyl acrylate	
% styrene[a]	M_n	PD	M_n	PD
90	9 400	1.13	9 500	1.14
80	8 800	1.23	9 000	1.22
70	8 100	1.29	7 800	1.33
60	7 100	1.32	8 000	1.29
50	6 600	1.49	6 900	1.44
40	6 800	1.60	6 400	1.52
30	6 400	1.67	6 500	1.65

[a] Molar percentage of styrene in the feed mixture.

Scheme 1



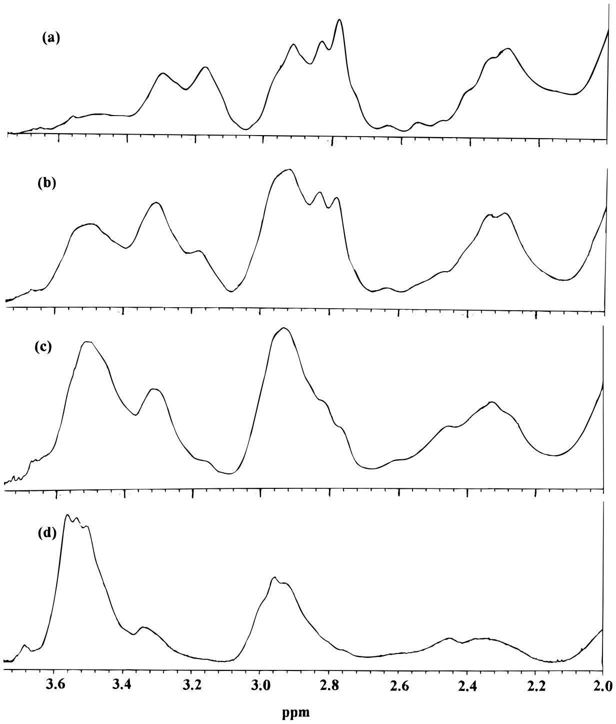
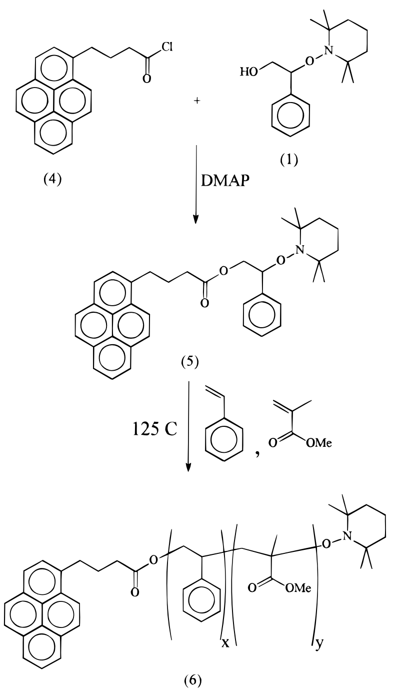


Figure 1. Comparison of the 300 MHz ^{1}H NMR spectra (2.00–3.80 ppm) of various random copolymers of styrene and methyl methacrylate: (a) 80/20 styrene/MMA; (b) 60/40 styrene/MMA; (c) 50/50 styrene/MMA; (d) 30/70 styrene/MMA.

in the sequence distribution of the styrene and methyl methacrylate repeat units as their relative percentage in the feed varies. For example, the large set of peaks at 3.4–3.6 ppm in the 30/70 styrene/methyl methacrylate copolymer (Figure 1d) is primarily due to the MMM triad, and as the relative percentage of styrene increases, the size of this peak becomes progressively smaller until it nearly vanishes in the 80/20 styrene/methyl methacrylate copolymer (Figure 1a). It is noteworthy that the observed changes in the methoxy group resonances for the random copolymers prepared by living free-radical polymerization essentially match the experimental and theoretical results that have been reported by a variety of groups for classically prepared styrene/methyl methacrylate random copolymers.[13,14] Using the procedure of Uebel,[14] the tacticity of the random copolymers, **3**, was also shown to be the same as that for classically prepared random copolymers. It can therefore be concluded that the random copolymers prepared by living free-radical polymerization have the same sequence distribution and tacticity as those prepared by normal free-radical methods. This is consistent with a recent report by Matyjaszewski[15] that poly(methyl methacrylate) prepared by Cu(I)-mediated living free-radical procedures has the same tacticity as poly(methyl methacrylate) prepared by a classical free-radical initiator (AIBN).

Scheme 2



Another advantage of living free-radical polymerizations is that the chain ends can be controlled to a degree previously only obtainable with more demanding techniques such as anionic polymerizations. The extent of chain end control in random copolymers prepared by TEMPO-mediated living free-radical polymerizations was investigated by the preparation of styrene/methyl methacrylate copolymers in which a single chain end is labeled with pyrene. The choice of pyrene as an end group was prompted by its extensive use in the preparation of polymers with fluorescent labels[16] and the ability to evaluate the percent of label incorporation by both UV–vis and ^{1}H NMR spectroscopy. The unimolecular initiator **5** was prepared by esterification of pyrene-1-butyryl chloride (**4**) with **1** in the presence of 4-(dimethylamino)pyridine. Purification by flash chromatography gave **5** as a light yellow oil in 82% yield, which was easily characterized and shown to be stable to prolonged exposure to both air and moisture. A variety of styrene/methyl methacrylate mixtures were then polymerized using **5** as an initiator. The presence of the pyrene label was shown to have no effect on the polymerization reaction, and the random copolymer **6** was shown to have the same sequence distribution and tacticity as the unlabeled material. The presence of the single pyrene label at the chain end was confirmed by both UV–vis and ^{1}H NMR spectroscopy. For example, copolymerization of 100 equiv of styrene/methyl methacrylate (8:2 molar ratio) gave the random copolymer **6** with a number-average molecular weight of 8300 amu and a polydispersity of 1.18. Using this value and an extinction coefficient (in THF) of 43 000 for the pyrene derivatives, **4** or **5**, analysis of the UV−vis spectrum of **6** showed that greater than 95% of the polymer chains contain a single pyrene group at the chain end. This high level of incorporation was also supported by the results of proton NMR analysis. Interestingly, treatment of the corresponding hydroxy-terminated random copolymer **3** with an excess of pyrene-1-butyryl chloride (**4**) was also shown to give the pyrene-labeled random copolymer **6**. In this case, the extent of label incorporation was only 80−85%, which demonstrates the effectiveness of using functionalized unimolecular initiators such as **5**.

In conclusion, we have demonstrated that the TEMPO-mediated living free-radical polymerization procedure is applicable to the preparation of a wide variety of well-defined random copolymer systems with low polydispersities and controlled molecular weights. For random copolymers of styrene and methyl methacrylate, the sequence distribution of the monomer units is essentially the same as that found for classical free-radical systems. Unlike traditional systems the chain ends could be accurately controlled and by the use of functionalized unimolecular initiators a single pyrene group could be introduced at the chain end of a styrene/methyl methacrylate random copolymer with greater than 95% efficiency.

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(9) The theoretical value is based on the relative molar ratio of initiator and monomer and the assumption that one molecule of initiator initiates a single chain with no termination; for different styrene ratios, the number of molar equivalents of monomer was adjusted to give a theoretical molecular weight of 9500 amu.

(10) M_n values were determined experimentally by size exclusive chromatography using commercially available narrow molecular weight polystyrene samples as standards.

(11) The use of homopolymer polystyrene standards in calculating the number-average molecular weights may contribute to the increasing discrepancy between the observed molecular weights and the theoretical molecular weights.

(12) The copolymerization of styrene and *p*-(chloromethyl)styrene has also been accomplished by the Xerox group, giving narrow polydispersity polymers. Georges, M., personal communication.

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