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Narrow Molecular Weight Resins by a Free-Radical Polymerization Process

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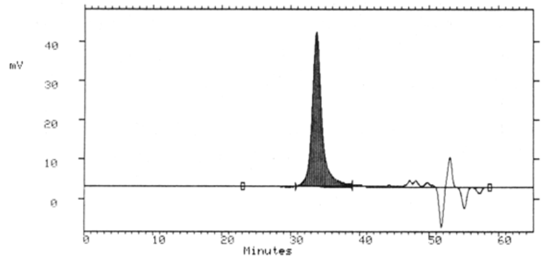
A primary goal of free-radical polymerization reactions has recently been achieved with the introduction of iniferters to provide "living" free-radical propagating chains.[1] However, the goal of synthesizing narrow polydispersity resins by a free-radical polymerization process remains elusive.[2] We report, herein, that narrow molecular weight resins have been synthesized by a new free-radical polymerization process with polydispersities (PDs) comparable to those that can be obtained by anionic polymerization processes and below the theoretical limiting polydispersity of 1.5 for a conventional free-radical polymerization process.[3]

Narrow polydispersity resins, in principle, may be obtained by a free-radical polymerization process if the process proceeds by a living mechanism, with no premature termination, and if all the propagating chains are initiated at about the same time, similar to what occurs in an anionic polymerization process. While we considered using iniferters to provide a living free-radical polymerization system,[4] molecular orbital calculations[5] indicated that stable free radicals, such as nitroxides, would yield adducts having weaker bonds with a propagating styrene chain than, for example, the sulfur free radicals formed by the dissociation of iniferters. It was, therefore, anticipated that stable free radicals, like nitroxides, could function to form thermally transient adducts in a similar manner to the iniferters[6] but with some added advantages. Nitroxide stable free radicals are well-known as free-radical inhibitors and are not known to initiate polymerization.[7] Consequently, there would be little concern with the stable free radicals initiating new chains late in the polymerization process as they reversibly react with a propagating chain. Furthermore, nitroxide stable free radicals have been shown to promote the dissociation of peroxide initiators[8] and, therefore, could contribute to enabling all the polymeric chains to initiate at the same time.



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Number Average            7873           Weight Average        9989
Peak Molecular Weight     10273          Dispersity            1.268785
Z avg / W avg             1.174933
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Figure 1. GPC of polystyrene showing narrow polydispersity.

Table I. Polymerization of Styrene (TEMPO/BPO = 1.2)

sample	convn (%)	rxn time (h)	M_n (10^{-3})	M_w (10^{-3})	PD
I	20	21	1.7	2.2	1.28
II	51	29	3.2	4.1	1.27
III	76	45	6.8	8.2	1.21
IV	90	69	7.8	10.0	1.27

Table II. Polymerization of Styrene as a Function of the TEMPO/BPO Ratio

sample	TEMPO/BPO	convn (%)	M_n (10^{-3})	M_w (10^{-3})	PD
I	0.5	86	45.6	71.7	1.57
II	1.5	74	33.1	41.1	1.24
III	3.0	71	18.2	21.7	1.19

The new process comprises heating a mixture of monomer or monomers, free-radical initiator, and a stable free radical. Reaction of styrene with benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), under argon, at 95 °C for 3.5 h, followed by heating at 123 °C for 69 h yielded a polystyrene (sample IV, Table I) with a polydispersity of 1.26 (Figure 1). Samples were extracted from the reaction mixture over the course of the reaction at the times indicated. The gel permeation chromatography (GPC) results and the percent conversion for each sample are summarized in Table I. Note that a narrow polydispersity was obtained early in the reaction, an indication that the polymeric chains were all initiated

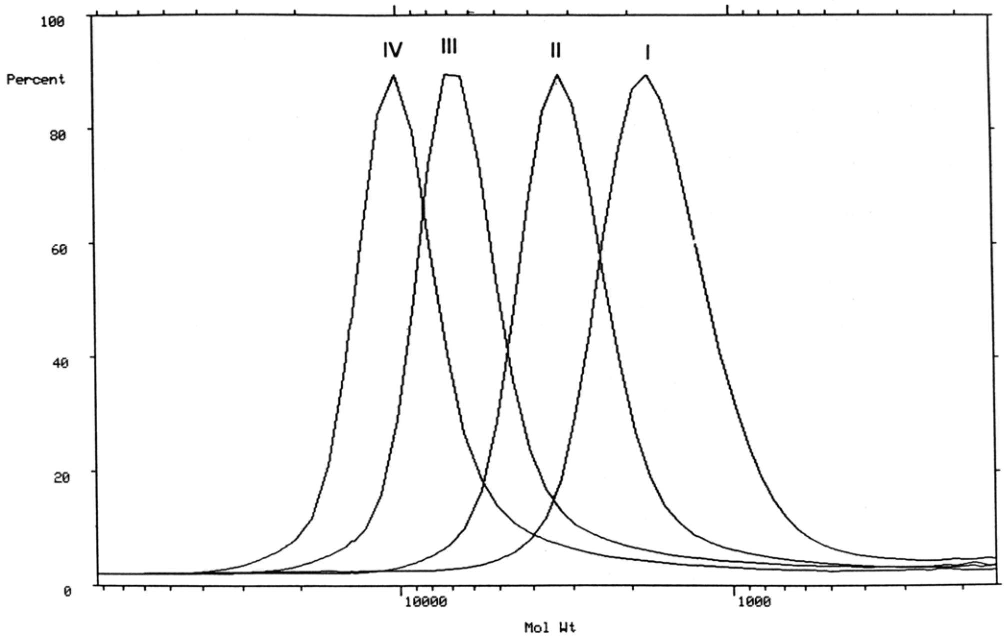

Figure 2. GPCs of polystyrene samples I–IV, from Table I showing the incremental increase of molecular weight with time with no concomitant broadening of the distribution.

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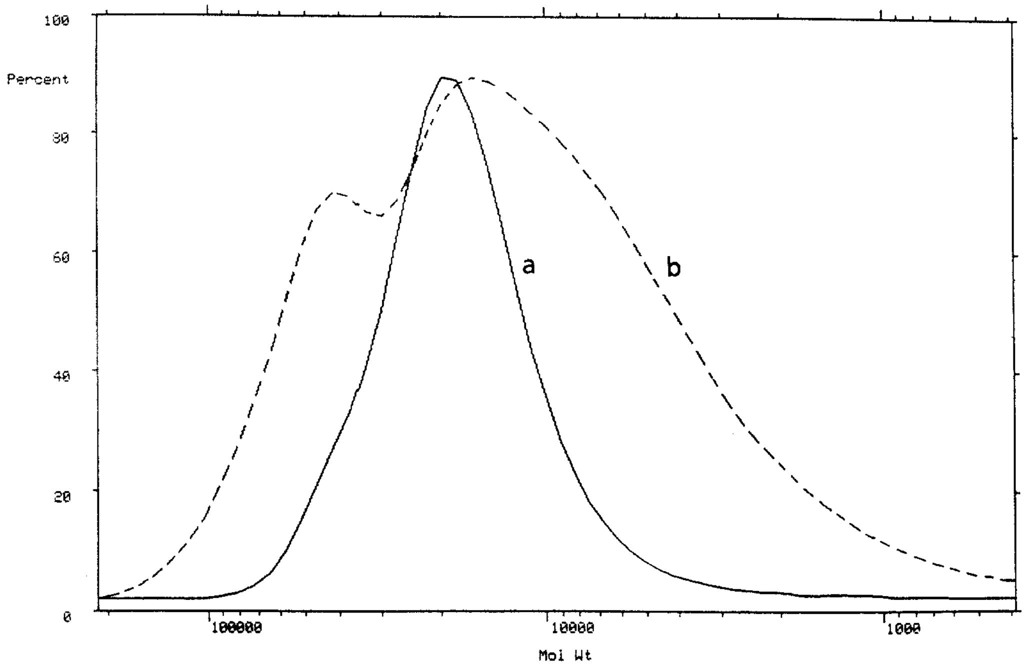

Figure 3. GPCs of poly(styrene-*co*-butadiene) prepared by a suspension process: (a) a narrow polydispersity resin prepared using TEMPO to reversibly cap the propagating chains; (b) a control resin prepared by a conventional suspension free-radical polymerization process.

at about the same time. The polydispersity remains constant over the entire course of the reaction, suggesting the reaction is proceeding via a type of living chain mechanism. The living nature of the propagating chains is further evident by the incremental increase in molecular weight with time (Figure 2). The narrow polydispersity is maintained even at very high monomer to polymer conversions. Similar results are obtained if the initial heating at 95 °C for 3.5 h, as described above, is eliminated and the reagents are simply reacted together at temperatures between 125 and 150 °C. Molecular weights as high as 150 000 have been achieved while maintaining polydispersities of 1.3 or less.

A suspension copolymerization of styrene (86% by weight) and butadiene with BPO and TEMPO yielded a copolymer with a PD of 1.36. In contrast, a control reaction, with no TEMPO, gave a copolymer with a PD of 4.21.[9] The molecular weight distributions of the two resins are compared in Figure 3.

The molar ratio of TEMPO to BPO affects both the reaction rate and the polydispersity of the resins formed as illustrated in Table II. The higher the ratio, the slower the reaction but the narrower the polydispersity. Lower molecular weight resins are also obtained with higher TEMPO/BPO ratios, an indication of increased initiator efficiency, a result that is under further investigation.

In conclusion, narrow polydispersity resins have been synthesized by a free-radical polymerization process that can be performed in solution, bulk, or suspension. Various features of the reaction and a means for significantly increasing the reaction rate, while maintaining narrow polydispersities, will be described in subsequent publications. Details describing the application of this process to the synthesis of block copolymers in which each block segment has a narrow polydispersity and a well-defined chain length are also forthcoming.

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