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Chain Transfer to Polymer: A Convenient Route to Macromonomers

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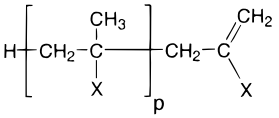
Macromonomers, possessing a 1,1-disubstituted alkene end group (see structure **1**), are versatile intermediates which have applications as transfer agents for molecular weight control[1−3] and have also seen widespread use as precursors to block[1,4] and graft copolymers.[3,5]



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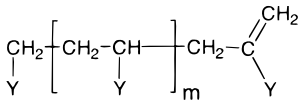
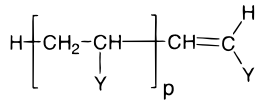
Two effective and well-known methods for the preparation of macromonomers are the use of radical addition−fragmentation chain transfer agents (e.g., allyl sulfides)[6] and catalytic chain transfer (CCT) with cobalt complexes.[7−10] Recently, the scope of the CCT process has been expanded by demonstrating how cobalt complexes can be used to prepare macromonomers based on, among others, acrylates and styrene by copolymerizing these monomers in the presence of α-methyl-substituted comonomers, such as α-methylstyrene and methyl methacrylate.[11] We now wish to report on a new process leading to macromonomers of structure **2** and **3** based on monosubstituted monomers which does not require the use of an added chain transfer agent or an α-methyl-substituted vinyl monomer as comonomer.[12] In this communication, we describe the preparation of polyacrylate and polystyrene macromonomers using this process.



2. Y = CO_2R
3. Y = Ph



4. Y = CO_2R
5. Y = Ph

The method is clean, simple, and economical and involves heating a mixture of either acrylate or styrene monomer in an appropriate solvent with an azo or peroxy initiator at elevated temperatures, typically >150 °C. Under these conditions, macromonomers of high purity can be prepared (Table 1 and Figure 1). However, reaction temperatures are not restricted to above 150 °C, and with appropriate choice of monomer concentration, we have prepared polyacrylate macromonomers at temperatures in the range 80−240 °C (Table 1).[13] The vinyl end-group structures of macromonomers **2** and **3** were established by comparing the ^{1}H NMR chemical shifts of the vinyl end groups with those of ω-unsaturated methyl methacrylate trimer[14] and polystyrene macromonomer, respectively.[6] The presence of structures **4** and **5** was not detected by ^{1}H NMR.[15] The "purity" of macromonomers is defined as the relative amount of macromonomer compared to nonmacromonomer products (i.e., products from radical−radical termination or chain transfer). This ratio can be determined from the analysis of the ^{1}H NMR spectrum by comparison of the integrals of the alkene end group and those of the butyl ester for poly(*n*-butyl acrylate) or phenyl for polystyrene macromonomers (Figure 1). The molecular weight obtained in this way is compared with that obtained from the GPC chromatogram. The reported molecular weights for poly(butyl acrylate) macromonomers were determined by the universal calibration method, using literature Mark−Houwink constants.[16,17] Polystyrene standards were used to calibrate the system. The results in Table 1 show that under our conditions byproducts are minimal and that macromonomers of >90% purity are typically achieved.

This method is not limited by the type of acrylate ester group. The results in Table 1 show that poly(methyl acrylate) and poly(benzyl acrylate) macromonomers can be prepared in high purity. Similarly, the nature of the solvent appears to have no marked effect on this chemistry.

The pathway that could lead to macromonomer formation is outlined in Scheme 1. The key steps in the mechanism are believed to be chain transfer to polymer backbone to give intermediate radical **6** and β-scission to give the observed macromonomer along with a new propagating radical. Fragmentation by β-scission is a well-known process[2] and is the basis for radical addition−fragmentation chain transfer.[6] Similarly, chain transfer to polymer backbone in acrylate polymerizations is a known process and was the subject of a recent study on the synthesis of branched polyacrylates.[18] In that study, the backbone derived radical (viz. **6**) gave monomer addition leading to branching; macromonomer formation was not reported. Chain transfer to polymer backbone can, in principle, occur via two different pathways: (i) through an intramolecular H abstraction (backbiting) or (ii) through an intermolecular H abstraction.[19] To help determine the predominant mechanism, an experiment was performed whereby dimethyl 2,2′-azobis(isobutyrate) was fed into a mixture of poly(butyl acrylate) ($\bar{M}_n \sim 100\,000$) and *n*-amyl acetate, heated at 150 °C. We observed no change in the $\bar{M}_n$ of the poly(butyl acrylate), and no poly(butyl acrylate) macromonomer was detected. In a second experiment, preformed poly(butyl acrylate) polymer ($\bar{M}_n \sim 110\,000$, PD ~ 1.1) was added to a 10 wt % *n*-butyl acrylate solution in *n*-butyl acetate and heated at 150 °C with 2,2′-azobis(2-methylpropane). Under these conditions, poly(butyl acrylate) macromonomer ($\bar{M}_n \sim 1960$, PD ~ 1.75) was obtained (cf. Table 1), and no change in the preformed poly(butyl acrylate) polymer ($\bar{M}_n \sim 110\,000$, PD ~ 1.1) was observed. These results suggest that at lower monomer concentration the backbiting mechanism is the predominant pathway for backbone H abstrac-

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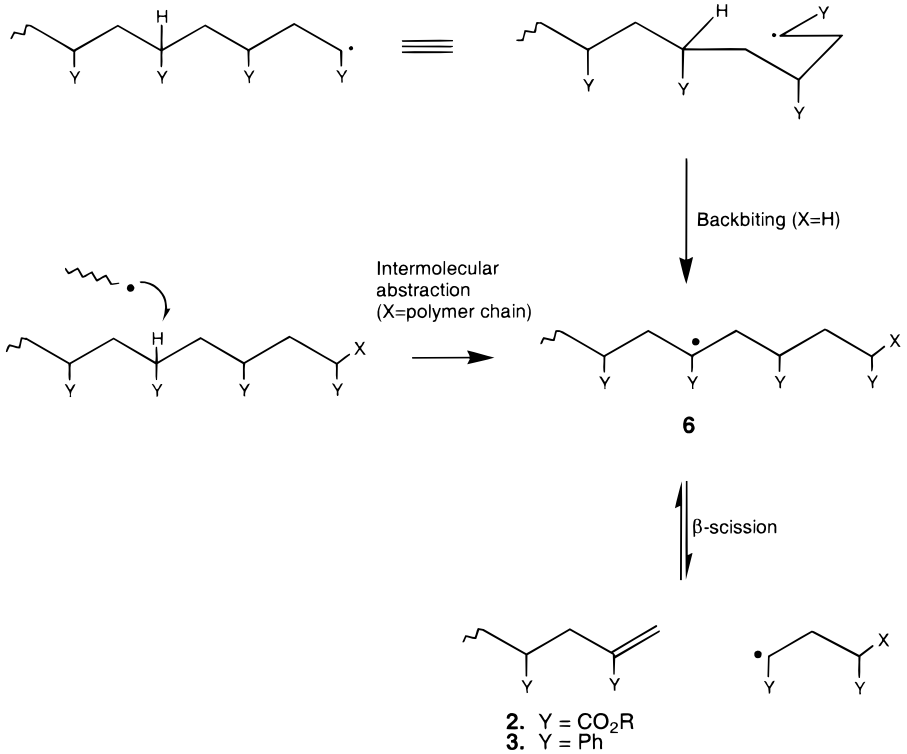
Table 1. Preparation of Polyacrylate and Polystyrene Macromonomers by Batch Polymerization under Various Conditions

macromer	[monomer], wt %	solvent[h]	temp, °C	time	% conv	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	macromer purity,[i] %
pBA[a]	25	nBuAc	150	20 min	65	2000	2.40	>90
pBA[a]	40	nBuAc	150	20 min	82	4530	2.95	>90
pBA[a]	60	nBuAc	150	20 min	90	10610	2.50	>90
pBA[b]	1.5	toluene	80	70 min	6	1770	2.00	>90
pBA[c]	5	toluene	110	80 min	5	2300	1.70	>90
pBA[d]	25	nBuAc	240	20 min	100	1310	1.80	~85
pBA[e]	25	nBuOH	220	20 min	96	1170	1.80	>90
pBA[f]	11	nBuAc	150	8 h	4	2250	1.90	>90
pMA[f]	11	nBuAc	150	8 h	3	1930	2.20	>90
pBzA[f]	11	nBuAc	150	8 h	7	2220	2.00	>90
pS[g]	5	nAmAc	170	7 h	99	3090	1.90	>90

[a] *n*-Butyl acrylate in *n*-butyl acetate was heated with 1×10^{-4} M 2,2′-azobis(2,4,4-trimethylpentane). [b] *n*-Butyl acrylate in toluene was heated with 5.2×10^{-6} M 2,2′-azobis(2,4-dimethylvaleronitrile). [c] *n*-Butyl acrylate in toluene was heated with 1.7×10^{-5} M 1,1′-azobis(1-cyclohexanecarbonitrile). [d] *n*-Butyl acrylate in *n*-butyl acetate was heated with 1.17×10^{-4} M cumene hydroperoxide. [e] *n*-Butyl acrylate in *n*-butanol was heated with 1.5×10^{-4} M cumene hydroperoxide. [f] The indicated monomers were treated under identical conditions by heating with 6.9×10^{-5} M 2,2′-azobis(2-methylpropane). [g] Styrene in *n*-amyl acetate was heated with 3×10^{-4} M 2,2′-azobis(2-methylpropane). [h] nBuAc, *n*-butyl acetate; nBuOH, *n*-butanol; nAmAc, *n*-amyl acetate. [i] See text for calculation method.

Scheme 1. Mechanism of Macromonomer Formation



tion. However, at higher monomer concentration the intermolecular mechanism may become more important.[18]

The molecular weight of the macromonomer can be controlled by varying the reaction temperature. The results in Table 1 show that, at a specific monomer concentration (e.g., 25 wt % BA), increasing the reaction temperature from 150 to 240 °C reduces the $\bar{M}_n$ from 2000 to 1310. Under our conditions, if all radicals **6** (formed by any mechanism) undergo fragmentation, then the molecular weight of the polymer will be determined by the incidence of backbone abstraction. In ethylene homopolymerization it is known that increasing the reaction temperature increases the incidence of backbone hydrogen abstraction.[20−22] This trend is likely to apply to acrylate and styrene homopolymerizations. Consequently, higher reaction temperatures are likely to increase the incidence of backbone methine hydrogen abstraction and also increase the incidence of fragmentation. This has the overall effect of decreasing the molecular weight of the polymer.

Similarly, monomer concentration can be used to alter the molecular weight of the macromonomer. The results in Table 1 show that decreasing the concentration of *n*-butyl acrylate from 60 to 25 wt % decreases the $\bar{M}_n$ from 10 610 to 2000. A lower monomer concentration reduces the rate of propagation, thereby leading to macromonomers of lower molecular weight. We have also observed an increase in branching of the macromonomers as monomer concentration increases. This is in accordance with a recent report.[18] There are two possible routes to increased branch formation: (i) copolymerization of the macromonomer and/or (ii) monomer addition to radical **6**.

The results presented in Table 1 clearly show that an abstraction−fragmentation process as outlined in Scheme 1 is a significant pathway leading to macromonomer formation during acrylate polymerization.

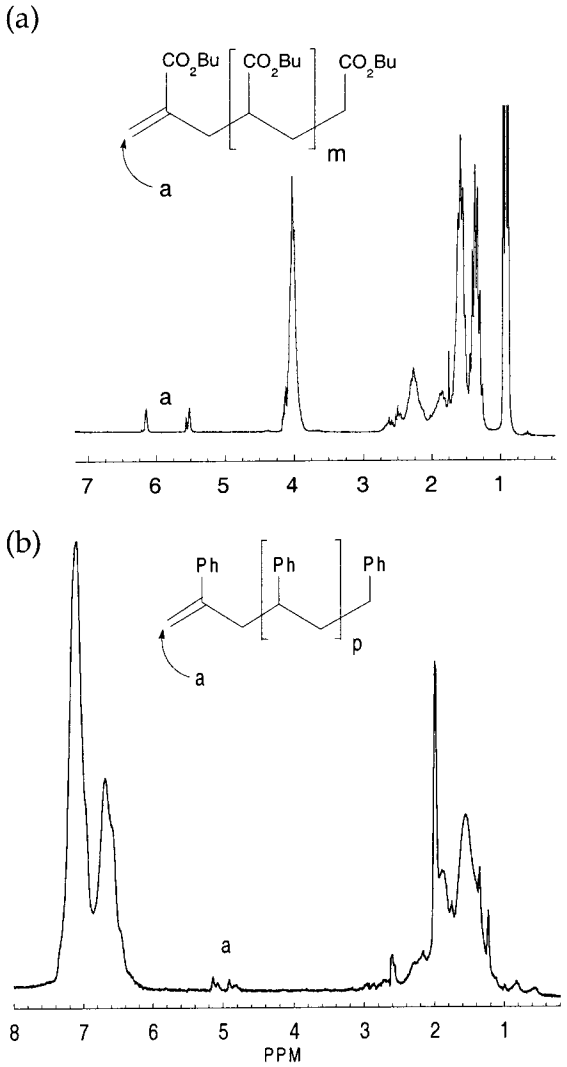


Figure 1. ^{1}H NMR spectrum of (a) poly(*n*-butyl acrylate) macromonomer ($\bar{M}_n = 1570$) in deuterated chloroform. The 1,1-disubstituted alkene end group is identified by signals at δ 6.2 and 5.5 ppm. (b) Polystyrene macromonomer ($M_n = 3090$) in deuterated acetone. The 1,1-disubstituted alkene end group is identified by signals at δ 5.1 and 4.8 ppm.

Since we have shown that this chemistry occurs at temperatures of 80 °C and above (and most likely below 80 °C), it may provide the reason that the determination of Arrhenius parameters and propagation rate constants for acrylate polymerizations leads to irreproducible results[23] except at very low temperatures.[24,25] These findings also help to explain why kinetic parameters available in the literature tend to significantly uunderestimate the molecular weight of poly(butyl acrylate) polymers at high reaction temperatures.

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