cumulated renormalization group results for a semidilute solutions, we could explicitly calculate various quantities semiquantitatively which are consistent with the scaling results (without entanglement effects). We stressed that there are two overlap parameters, static and dynamical (X and Y in our paper). Comparing our results with experiments, we concluded that there is no semidilute solution without entanglement; as soon as the overlap parameter becomes positive, there is an entanglement effect. At this point, we failed to quote important experimental results by Adam and Delsanti,[3] which clearly demonstrated for the first time that even with entanglements dynamical quantities are functions of the overlap parameter. We apologize to Professors Adam and Delsanti for this regrettable omission.

Acknowledgment. Y.O. is grateful to M. Adam for very useful conversations. The work is, in part, supported by the National Science Foundation Grant DMR 87-01393.

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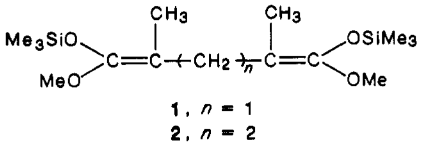
Received May 25, 1988

Group Transfer Polymerization by Bifunctional Initiators: A Simple Method for ABA Triblock Copolymers

In 1983 Du Pont announced a new method of a living polymerization termed group transfer polymerization (GTP).[1] Polar monomers, especially methacrylate and acrylate, may be polymerized by special initiators with a silicon-containing group in the presence of nucleophilic or electrophilic catalyst to polymers with controlled molecular weights and narrow molecular weight distributions. GTP is a living polymerization because chain transfer and termination reactions are virtually absent.[1,4,5] Upon addition of a second monomer the living ends propagate, further enabling the chemist to synthesize block copolymers. Recently, it was reported that an ABA triblock copolymer was prepared by a difunctional initiator, silyl ketene acetal of ethylene glycol diisobutyrate.[2]

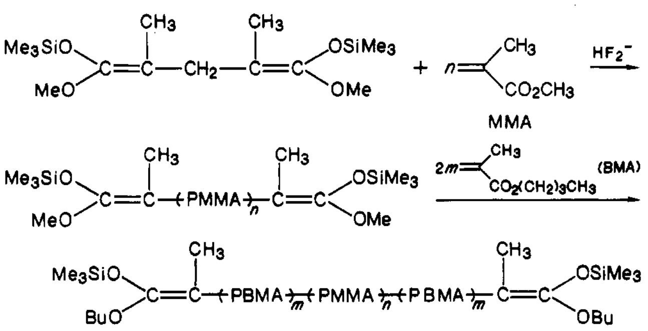
We report here the synthesis of a new type of difunctional initiators, [1,5-dimethoxy-2,4-dimethyl-1,5-bis[(trimethylsilyl)oxy]-1,4-pentadiene (**1**) and [1,6-dimethoxy-2,5-dimethyl-1,6-bis[(trimethylsilyl)oxy]-1,5-hexadiene (**2**), and the polymerization of various acrylic monomers using them.



1, $n = 1$
2, $n = 2$

1 was prepared by general procedure from dimethyl 2,4-dimethylglutarate;[3] yield 75%, bp 84 °C (0.1 Torr).

Scheme I



Anal. Calcd for $C_{15}H_{32}O_4Si_2$: C, 54.17; H, 9.70; Si, 16.89. Found: C, 53.51; H, 9.85; Si, 16.88. IR 1700 cm^{-1} (C=C); ^1H NMR ($CDCl_3$, 60 MHz) δ 0.2 (s, 18 H, Me_3Si), 1.5 (s, 6 H, CH_3), 2.7 (s, 2 H, CH_2), 3.6 (s, 6 H, OCH_3); ^{13}C NMR ($CDCl_3$, 80 MHz) δ 148.2 (=CO_2), 94.0 (>C=), 55.2 (OCH_3), 30.2 (CH_2), 12.0 (CH_3), −1.8 ($OSiMe_3$). On the other hand, **2** could not be synthesized from the procedure because ring closure reaction (Dieckmann reaction) occurred predominantly. However, **2** was prepared in good yield by modification of the procedure. For example, lithium diisopropylamide prepared from diisopropylamine (0.2 mol) and n-butyllithium (0.2 mol) at −30 °C was added dropwise to the mixture of dimethyl 2,5-dimethyladipate (20.2 g, 0.1 mol) and chlorotrimethylsilane (50 mL, 0.5 mol) in tetrahydrofuran at −78 °C. After the mixture was stirred for 30 min, it was filtered and the solvent was evaporated. Then the residue was fractionally distilled under reduced pressure to give 24.5 g of **2** (yield 70%): bp 87–88 °C (0.1 Torr). Anal. Calcd for $C_{16}H_{34}O_4Si_2$: C, 55.44; H, 9.87; Si, 16.21. Found: C, 55.98; H, 10.22; Si, 15.97. IR 1705 cm^{-1} (C=C); ^1H NMR ($CDCl_3$, 60 MHz) δ 0.2 (s, 18 H, Me_3Si), 1.4 (s, 6 H, CH_3), 1.8 (s, 4 H, CH_2CH_2), 3.4 (s, 6 H, OCH_3); ^{13}C NMR ($CDCl_3$, 80 MHz) δ 148.2 (=CO_2), 93.8 (>C=), 55.2 (OCH_3), 28.6 (CH_2), −1.8 ($OSiMe_3$), 12.0 (CH_3).

The characteristic band of ester at 1740–1750 cm^{-1} was absent in IR spectra of **1** and **2**, which confirmed the absence of ester impurities.

The polymerization was carried out under a positive dry argon atmosphere at room temperature by using glassware previously dried at 150 °C for 24 h. Tetrahydrofuran (THF, dried with $LiAlH_4$) was used as solvent and tris(dimethylamino)sulfonium bifluoride ($TASHF_2$)[1] as catalyst. For example, a 50-mL reactor fitted with an argon inlet, a stirrer, and thermocouple was charged with THF (8 mL), $TASHF_2$ (0.16 mL, 0.1 M in CH_3CN), and initiator **1** (0.23 mL, 0.68 mmol). Then methyl methacrylate (0.8 mL) was added via a syringe pump over 2 min. An hour after, a 3-mL aliquot was evaporated and the residue dried to give 0.26 g of PMMA ($\bar{M}_n$ = 2200, $\bar{M}_w$ = 2500). To the rest of the mixture butyl methacrylate (1.6 mL, 10.13 mmol) was added. The mixture was stirred for an additional 3 h and then treated with methanol (4 mL). Removal of the solvent in vacuo gave 1.92 g of the copolymer; $\bar{M}_n$ = 7200, $\bar{M}_w$ = 8700, and D = 1.21 (theoretical MW ≈ 4380) (Scheme I). It was found that the elution curve of the copolymer in GPC was unimodal without shoulders as shown in Figure 1, and DSC showed two T_g's at 35 and 115 °C. The expected composition of 33 mol % of MMA and 67 mol % of BMA was confirmed by ^1H NMR analysis. There is a possibility of forming a trace of homopolymer B or diblock copolymer AB via termination reactions with, e.g., moisture. Formic acid which is a solvent of PMMA and nonsolvent of PBMA[6] was chosen as a solvent to separate homopolymer from copolymer. Little decrease (ca. <2%) in weight of copolymer, however, was observed

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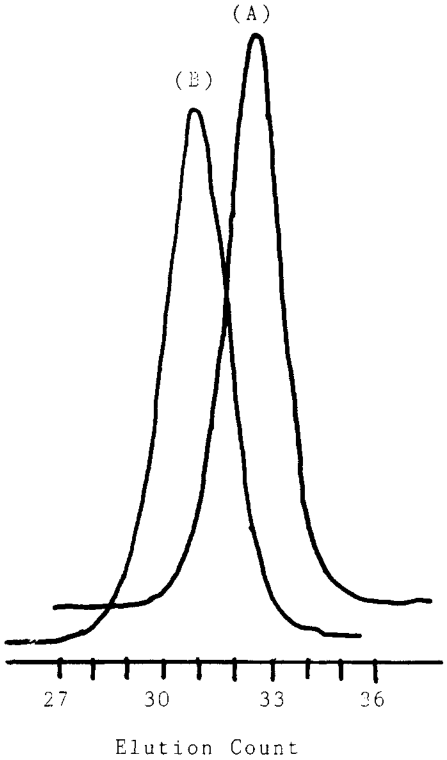

Figure 1. GPC curves for poly(methyl methacrylate) (A) and for poly(butyl methacrylate-*block*-methyl methacrylate-*block*-butyl methacrylate) (B): peak A, $\bar{M}_n$(obsd) = 2200, $\bar{M}_w/\bar{M}_n$ = 1.14; peak B, $\bar{M}_n$(obsd) = 7200, $\bar{M}_w/\bar{M}_n$ = 1.21.

Table I
Polymers by GTP with Initiators 1 and 2

expt[a]	monomer[b] (mmol)	initiator (mmol)	calcd MW	obsd[c]		D (=$\bar{M}_w/\bar{M}_n$)
				$\bar{M}_n$	$\bar{M}_w$	
1	MMA (7.5)	**1** (0.68)	1390	2200	2500	1.14
2	BMA (14.6)	**2** (0.33)	6110	9910	12190	1.23
3	AMA (13.5)	**2** (0.33)	5200	8370	10130	1.21
4	1. MMA (4.9) 2. BMA (10.1)	**1** (0.44)	4380	7200	8710	1.21
5	1. BMA (7.0) 2. MMA (7.0)	**2** (0.33)	5040	8160	10360	1.27
6	1. MMA (6.0) 2. MA (12.0)	**1** (0.34)	4850	7290	9550	1.31
7	1. AMA (4.5) 2. MMA (15.9)	**1** (0.34)	6350	9860	12720	1.29
8	1. MMA (7.0) 2. AMA (8.0)	**2** (0.33)	5080	8380	10640	1.27
9	1. AMA (4.6) 2. HEMA[d] (8.3)	**1** (0.34)	6660	11340	14180	1.25

[a] Catalyst: TASHF$_2$, 0.06 mL (0.1 M in CH$_3$CN). Solvent: THF, 5 mL (except to experiments 1 and 4). Yield, all quantitative. [b] AMA, allyl methacrylate, MA, methyl acrylate; (1) B block; (2) A block in ABA triblock copolymer. [c] Obtained from GPC (Waters Model 150 C) in THF by using polystyrene standards. [d] 2-(Trimethylsiloxy)ethyl methacrylate.

after stirring overnight. From the above result the product is considered to consist of ABA triblock copolymer.

The experimental data of homopolymers and ABA triblock copolymers with the difunctional initiator **1** and **2** are summarized in Table I. The degree of polymerization was controlled by the ratio of monomer to initiator. The molecular weights show narrow molecular weight distributions, typically D (=$\bar{M}_w/\bar{M}_n$) = 1.1–1.3. The experimental molecular weights of the polymers are about 50–70% higher than those of theory, which is probably due to the fact that values are calculated by a polystyrene calibration curve.

To confirm the structure of the "living" or silyl ketene acetal end group of the polymer, the oligo-PMMA was prepared with **2** as difunctional initiator. The peaks at 151.8, 95.5, 56.4, and 0.5 ppm which well correspond to those of **2** were exhibited in the ^{13}C NMR spectrum of the oligomer. Hence, the B-block is constructed first as a homopolymer with two living ends followed by addition of A-blocks to give an ABA triblock copolymer.

In conclusion, this difunctional initiator system provides a very useful method for the synthesis of ABA triblock copolymers by using GTP. A more detailed description of these and other studies related to difunctional initiators will be discussed elsewhere.

Registry No. 1, 115533-61-4; 2, 56920-00-4; TASHF$_2$, 85248-37-9; MMA (homopolymer), 9011-14-7; BMA (homopolymer), 9003-63-8; AMA (homopolymer), 25189-05-3; (MMA)(BMA) (block copolymer), 107404-23-9; (MMA)(MA) (block copolymer), 108150-11-4; (AMA)(MMA) (block copolymer), 115533-62-5; (AMA)(HEMA) (block copolymer), 115533-63-6; dimethyl 2,4-dimethylglutarate, 2121-68-8; lithium diisopropylamide, 4111-54-0; dimethyl 2,5-dimethyladipate, 19550-58-4; chlorotrimethylsilane, 75-77-4.

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Received October 26, 1987

Probing of the Ion Pair Association in Model Ionomers by Excimer Fluorescence

During the last two decades, ionomers, which are polymers containing a low concentration of charged units along the chain, have received an ever increasing interest.[1] The occurrence of thermoreversible ionic cross-links in the polymer dramatically changes some of its properties and opens the way to an extended range of applications. Among other effects, the ion pair association is responsible for the limited solubility of ionomers in nonpolar solvents. In low-polarity solvents, such as THF, ionomers, as examplified by a lightly sulfonated polystyrene (1–5 mol % sodium sulfonate), are, however, soluble and exhibit a solution behavior that strongly depends on polymer concentration.[2] Above a critical concentration ($C^\dagger$), approximately corresponding to polymer coil overlap (C^*), there is a marked increase in reduced viscosity, while below $C^\dagger$, the viscosity is significantly less than that of the starting polymer. It has been suggested that interpolymer association predominates above $C^\dagger$, while intramolecular as-

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