units to make τ_p/τ_p° dimensionless, and ν is the usual exponent relating the molecular weight and the radius of gyration R_g of the chain. It is to be noted that a does not vanish at the Θ temperature and that $\rho L^{d\nu-1}$ is proportional to ρ/ρ^* where ρ^* is the overlap concentration.[1] Furthermore it must be pointed out that eq 3 contains an explicit mode dependence.

In the derivation of eq 1, a screened hydrodynamic interaction has been used. Since the internal modes of the chain are of concern here, the characteristic length scale is shorter than the size of the polymer chain. For lengths shorter than R_g the hydrodynamic screening length ξ_H in dilute solutions has been shown[6-9] to scale as

$$\xi_H^{-2} \approx \rho L^{\nu(d-2)-1} \tag{4}$$

so that $(\tau_p/\tau_p^\circ) - 1$ is proportional (in this regime) to

$$\rho L^{d\nu-1} \approx \xi_H^{-2} l_1/q \tag{5}$$

because $l_1 \sim L^{2\nu-1}$ and $q \sim L^{-1}$. We have suppressed the p-dependence as the present argument does not involve p. The formula of eq 5 has previously been used to successfully predict the concentration dependence of relaxation times.

Shiwa et al. have questioned the correctness of eq 5 (see ref 3 of ref 15). In their discussion[15] of the initial concentration dependence of τ_p, Shiwa et al. have used the relaxation (eq 2.9 of ref 15)

$$\xi_H^{-2} \approx \rho \tag{6}$$

Their use of eq 6 for ξ_H^{-2} instead of eq 4 in eq 5 leads to a result in disagreement with eq 5. While eq 5 has been derived for the regime of length scales shorter than R_g, eq 6 is not valid in this regime. On the other hand, the calculation of ξ_H in the appropriate region of short length scales ($|\mathbf{k}|R_g \gg 1$, where $\mathbf{k}$ is the wave vector) leads in dilute solutions to (see eq 2.10 of Shiwa et al.)

$$\xi_H^2 \approx \frac{L}{\rho}\int_{\mathbf{k}} \frac{S_1(\mathbf{k},q)}{(\mathbf{k}^2 + \xi_H^{-2})} \approx \rho^{-1} L^{1-\nu(d-2)} \tag{7}$$

which is in agreement with eq 4 and hence with eq 5. Here S_1 is the double Fourier transform of the static structure factor. Notice that the q dependence of $S_1(\mathbf{k},q)$ must be accounted for in performing the integral of eq 7 since we are interested in length scales shorter than the size of the polymer. Thus the error in the work of Shiwa et al. originates from the inconsistent use of formulas for different regimes.

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Comments on "On the Screening of Hydrodynamic Interactions in Dilute Polymer Solutions"

In the preceding paper,[1] Muthukumar claims that our paper[2] contains conceptual errors which cause disagreements with previous theories and experimental results. Actually, his criticism is not directed to the main body of our paper, but to one of our footnotes criticizing his work on the nonlinear concentration dependence of relaxation times (i.e., ref 3 in our paper). Furthermore, his comments are confined to a minor part of the footnote, leaving the main points in the note intact. However, we must admit that we have misunderstood his theory in the linear regime. We apologize to Professor Muthukumar for this mistake.

His claim of our results being inconsistent with themselves is based on his misconception of our paper, and we feel that the content of his paper[1] is rather misleading. the essence of our footnote is: the quantity Q introduced by Muthukumar is a complicated nonlinear function of the polymer concentration (or the monomer concentration), so that the identification of Q through matching first-order terms in the concentration is insufficient to fix Q in the higher order expansion formula. Thus, we explicitly wrote, "Since Q is a complicated function of c, the identification (A) [i.e., Muthukumar's identification] is at best legitimate only in the regime with linear c-dependence". Muthukumar directs his criticism to our secondary five-line comment following this main point in the footnote. Our comment says that even in the linear order the identification is not correct, if we accept the relation "$\xi_H^{-2} \approx \rho$ as was assumed in *the* theory". The theory in this quotation means Muthukumar's theory. This is due to our misunderstanding of his theory. However, the essential part of our criticism is intact since the main target of his theory is not the linear regime but the nonlinear regime. Besides, it is trivial that the linear order is proportional to the overlap parameter, though Muthukumar explains this at length in his paper. Incidentally, just above eq 6 in his paper, he suggests that our formula (2.9) gives the wrong relation, (6). As is demonstrated by Muthukumar himself in his letter, (2.9) which is equivalent to (2.10) in our paper gives the answer he wants in the dilute limit. Actually, one of our main results is to go beyond this limit to yield, e.g., the scaling relation (3.6), i.e., $(\xi_H/R_g^\circ)^2 \sim X^{-2\nu/(d\nu-1)}$. Here R_g° is the radius of gyration in the dilute limit and X the overlap parameter.

Judging from the preceding paragraph, we feel we should reemphasize the content of our paper. First of all, we stressed that the starting point of the theory must be internally consistent and that we should try to eliminate ad hoc assumptions as much as possible. Results do not always justify the starting point, especially when the results are robust as the equation for viscosity, etc. Combining a mode–mode coupling theoretical approach and the ac-

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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.

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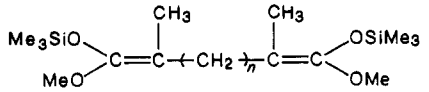
Group Transfer Polymerization by Bifunctional Initiators: A Simple Method for ABA Triblock Copolymers

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]

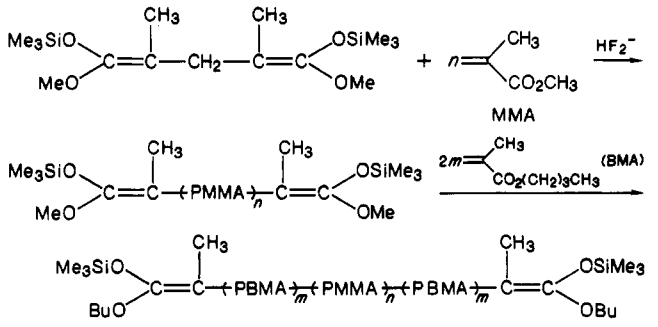
We report here the synthesis of a new type of difunctional initiators, [1,5-dimethoxy-2,4-dimethyl-1,5-bis-[(trimethylsilyl)oxy]-1,4-pentadiene (1) and [1,6-dimethoxy-2,5-dimethyl-1,6-bis[(trimethylsilyl)oxy]-1,5-hexadiene (2), and the polymerization of various acrylic monomers using them.



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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