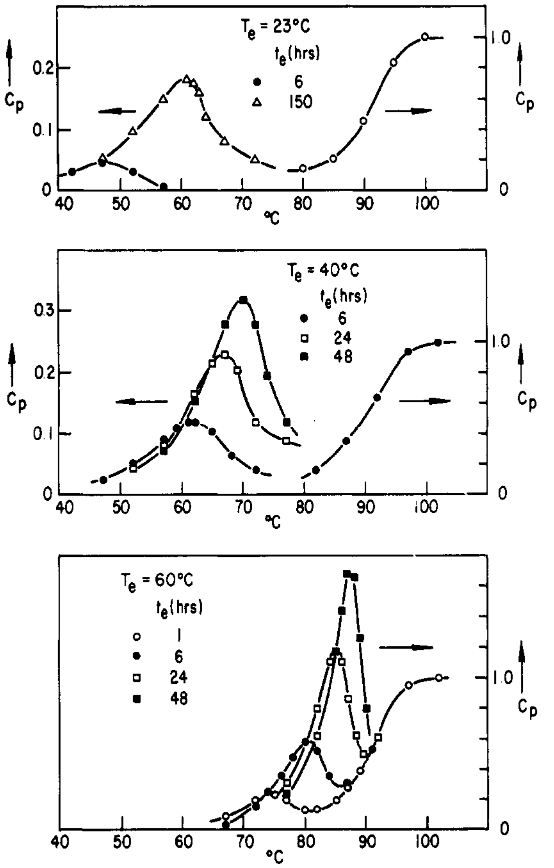


Figure 2. Model calculations of the normalized heat capacity for the combinations of T_e and t_e given in Figure 1. Parameters are ln $A = -274.0$, $\Delta H/R = 10^5$ K, and $\beta = 0.28$. The values of x are 0.325 at 23 °C, 0.365 at 40 °C, and 0.48 at 60 °C.

temperature after the following thermal history: holding at 120 °C for 30 min, plunging into liquid nitrogen (estimated cooling rate 10^3 K min^{-1}), heating to T_e and holding there for t_e, and cooling to room temperature. Annealing times varied from 1 to 48 h at room temperature, 40 °C, and 60 °C. The data are shown in Figure 1. To facilitate comparison with the predictions of eq 4, experimental heat capacity data were normalized to the dimensionless quantity C_p^{N} defined by the expression

$$C_p^{\mathrm{N}}(T) = \frac{C_p(T) - C_{pg}(T)}{C_{pe}(T) - C_{pg}(T)} \tag{5}$$

where C_{pg} is the glassy heat capacity well below the relaxation temperature range (linearly extrapolated into the transition range), and C_{pe} is the liquid (or rubber) heat capacity (similarly extrapolated). Thus, $C_p^{\mathrm{N}} = 0.0$ in the glassy state and $C_p^{\mathrm{N}} = 1.0$ in the rubbery state.

The calculated normalized heat capacities for the same combinations of T_e and t_e are shown in Figure 2. The thermal history used for the calculations was cooling from above T_g at 10^3 K min^{-1} to T_e, annealing for t_e, cooling to room temperature (300 K) at 10^3 K min^{-1}, and heating at 20 K min^{-1}. This approximation to the experimental history is considered adequate for testing the validity of the model.

The effects of varying t_e are reproduced by the model with a single set of values for the four parameters (A, ΔH, β, and x). However, reproduction of the effects of varying T_e requires that x increase with T_e. More recent work, to be detailed later,[12] indicates that this is due to neglect of the self-retarding kinetics during annealing, i.e., the simplification that during annealing $\tau_{0,e}$ is independent of time. Also, the parameter Δh^* was fixed by the quench rate dependence of T_g (estimated from preliminary data) and A fixed by the value of T_g. Thus only two parameters, β and x, were varied in fitting the model to the sub-T_g peaks. With the chosen values of Δh^* and A, the estimated uncertainties in β and x are ±0.01. Other values of Δh^* were not tried.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. CPE-7920740 under the Industry/University Cooperative Research Program. It is a pleasure to acknowledge useful discussions with Professor H. Hopfenberg of North Carolina State University and the experimental assistance of F. W. Kunig. We thank the BFGoodrich Co. for permission to publish this paper.

References and Notes

(1) Illers, K. H. *Makromol. Chem.* **1969**, *127*, 1.
(2) O'Reilly, J. M.; Mosher, R. A. *J. Appl. Phys.* **1980**, *51*, 5137.
(3) Wyzgoski, M. G. *J. Appl. Polym. Sci.* **1980**, *25*, 1455.
(4) Richardson, M. J.; Savill, N. G. *Br. Polym. J.* **1979**, *11*, 123.
(5) Schultz, A. R.; Young, A. L. *Macromolecules* **1980**, *13*, 663.
(6) Petrie, S. E. B. *J. Polym. Sci., Part A-2* **1972**, *10*, 1255.
(7) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097.
(8) Wunderlich, B.; Bodily, D. M. *J. Polym. Sci., Part C* **1963**, *6*, 137.
(9) Wunderlich, B.; Bodily, D. M.; Kaplan, M. H. *J. Appl. Phys.* **1964**, *35*, 95.
(10) De Bolt, M. A.; Easteal, A. J.; Macedo, P. B.; Moynihan, C. T. *J. Am. Ceram. Soc.* **1976**, *59*, 16.
(11) Sasabe, H.; Moynihan, C. T. *J. Polym. Sci.* **1978**, *16*, 1447.
(12) Hodge, I. M.; Berens, A. R., in preparation.

I. M. Hodge* and A. R. Berens
BFGoodrich Research and Development Center
Brecksville, Ohio 44141

Received March 16, 1981

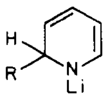
Anionic Polymerization of Methacrylates. Novel Functional Polymers and Copolymers

We report here, in preliminary form, methods we have developed for the synthesis of block and random methacrylate polymers and copolymers with well-defined compositions, many bearing functional groups incorporated either through the use of special initiators or by reaction of the living polymethacrylate anion with electrophiles.

Beginning in the 1950s, the pioneering work of Szwarc, Bywater, and Morton on the anionic polymerization of styrene and dienes introduced the concept of "living" polymers and demonstrated their great potential for the preparation of well-defined block copolymers and terminal-functional polymers. Subsequently, in the early 1960s, extensive interest in the anionic initiation of methacrylate polymerization began to develop. These studies dealt mainly with mechanisms, kinetics, and polymer configuration. In contrast to the polymerization of styrene and dienes, the anionic polymerization of methacrylates proceeds predictably only with careful selection of solvent, temperature, and initiator. In our synthetic work, we have investigated some of these aspects and have extensively applied nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and high-performance liquid chromatography to the characterization of our polymers.

We began by reinvestigating the work of Braun and co-workers.[1] Their prime interest was in the effect of solvent composition, temperature, and initiator counterion on the *configuration* of poly(methyl methacrylate)

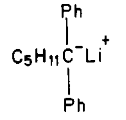
(PMMA) initiated with alkali metal *n*-alkyls. We found that the PMMA prepared by initiation with *n*-butyllithium in 30:70 (v/v) pyridine–toluene mixtures is essentially monodisperse and that the polymerization has the characteristics of a truly living system from −78 to as high as −20 °C, provided that the pyridine is present in large excess with respect to the alkyllithium. The M_n's of the products are then predetermined by the molar ratio of monomer to initiator. By NMR analysis of the polymer, we concluded that the actual initiator is not the alkyllithium but the dihydropyridine amide adduct (**1**) derived from pyridine and the alkyllithium.[2]



1

We found that the use of tetrahydrofuran (THF) as solvent with equimolar amounts of *sec*- or *tert*-butyllithium and pyridine to generate the initiator permitted easier isolation of the polymers and obviated the need for gross amounts of pyridine which might interfere with projected electrophilic reactions. In this system, the living character of the polymerization was maintained in the temperature range −78 to ca. −65 °C, but it was more temperature sensitive than the pyridine–toluene system so that termination became important at temperature above −65 °C. Moreover, in THF with alkyllithiums and pyridine, hindered alkyls must be used to maintain molecular weight control; *n*-butyllithium gave a broad-distribution product of unpredictable molecular weight. We obtained no polymer with alkyllithium reagents alone in THF.

The polymers obtained as described above have dihydropyridine end groups, which caused the polymers to yellow when heated above ca. 100 °C. Thermally stable end groups were obtained by the use of (1,1-diphenylhexyl)lithium (DPHLi, **2**) as initiator.[3] DPHLi was readily prepared in situ from equimolar *n*-butyllithium and 1,1-diphenylethylene at room temperature in THF. Polymerization of MMA was then conducted at −78 to −70 °C to obtain living polymers.

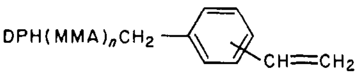


$$\underset{\text{Ph}}{\overset{\text{Ph}}{C_5H_{11}C^-Li^+}}$$

2

The aromatic protons of the diphenylhexyl initiating group in these polymers provide a valuable probe for determining degree of polymerization (DP) by proton NMR analysis. Assigning ten protons to the aromatic peak and comparing its integrated intensity with that of the ester methoxyl peak gave accurate and reproducible estimates of DP. The method is not only adjunct to GPC but is, in fact, more dependable than GPC for polymers with molecular weights up to about 10 000.

The living PMMA solutions react efficiently with electrophiles such as vinylbenzyl iodide or bromide and allyl bromide at −78 °C to form functionally capped polymers such as **3** and **4**.[4] For example, *n*-butyllithium (22 mmol, 1.6 M in hexane) was added to a solution of 1,1-diphenylethylene (22 mmol) in THF (150 mL, freshly distilled from benzophenone/sodium) under argon. The deep red solution was cooled to −78 °C and MMA (220 mmol) was added dropwise at such a rate that the temperature did not exceed −70 °C.



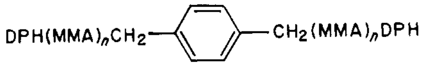
3

$DPH(MMA)_nCH_2CH{=}CH_2$

4

Allyl bromide (22 mmol) was added to the cold solution, which was stirred at −78 °C for 3 h. The polymer was precipitated in hexane and was recovered in quantitative yield; NMR, $M_n = 1400$; GPC, $M_n = 1300$, $M_w/M_n = 1.16$. NMR vinyl bands δ 4.80, 4.96, 5.12, 5.42, 5.52; integrated aromatic to vinyl intensity ratio 10:3 (theory 10:3).

The living polymer can be coupled at −78 °C with bis(bromomethyl)benzenes. For example, a polymerization with DPHLi (15 mmol) and MMA (150 mmol) was carried out as described above and a one-third aliquot was removed to obtain control polymer. To the remainder was added a THF solution of 1,4-bis(bromomethyl)benzene (5 mmol), the reaction was allowed to proceed for 10 min, and the polymer was isolated. The control had $M_n = 1000$ and $M_w/M_n = 1.11$ and the coupled product **5** had $M_n = 1800$ and $M_w/M_n = 1.06$; this increase corresponds to a coupling efficiency of about 90%.

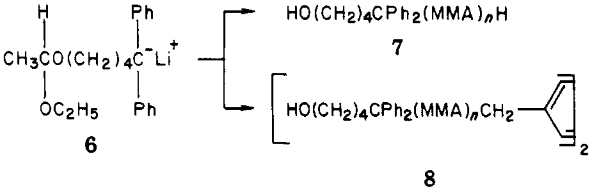


5

The control inherent in these polymerizations enabled us to tailor a series of polymers for correlation of T_g and melt flow with M_n and polydispersity. Thus for a series of essentially monodisperse, highly syndiotactic PMMA's the T_g of a sample with $M_n = 9000$ was 116 °C, which increased to a maximum of ca. 132 °C at $M_n = 45\,000$ and remained constant up to $M_n = 120\,000$. Rheological studies on similar monodisperse samples ($M_w/M_n = 1.04$–1.16) with an Instron melt rheometer demonstrated that Newtonian flow is maintained up to 300 s^{-1} when M_n is 25 000 and to at least 30 s^{-1} when M_n is 44 000. Melt flow for a sample with $M_n = 121\,000$ was non-Newtonian.

Anionic block copolymerization of methacrylates has been investigated by several groups.[5,6] We have further pursued this subject with a variety of methacrylates in block and random copolymers to determine the effects of comonomer composition and DP on molecular weight distribution and T_g. In many cases narrow molecular weight distributions were maintained while in others, more or less broadening occurred, depending on the structure of the comonomer. For example, a block of living PMMA was prepared and lauryl methacrylate (LMA) was added to it in portions to form an MMA-*b*-LMA diblock copolymer. To it in turn was added a final block of MMA to form a triblock copolymer. Aliquots were removed at various stages. The initial homo-PMMA had the nominal compositon $DPH(MMA)_{200}$, with $M_w/M_n = 1.32$ and $T_g = 109$ °C. An intermediate diblock copolymer, $DPH(MMA)_{200}$-*b*-$(LMA)_{67}$, had $M_w/M_n = 1.31$ and showed two T_g's at about −5 and +105 °C. A further intermediate diblock, $DPH(MMA)_{200}$-*b*-$(LMA)_{134}$, had a substantially broadened molecular weight distribution ($M_w/M_n = 1.72$) and three T_g's at −44, 0, and +104 °C. The final composition, $DPH(MMA)_{200}$-*b*-$(LMA)_{200}$-*b*-$(MMA)_{200}$, was further broadened in distribution ($M_w/M_n = 3.56$), but showed the same T_g's as the previous diblock product. There are at least two factors which contribute to broadening. One is the low solubility of LMA monomer in THF at −78 °C. The second is no doubt kinetic and probably related to inaccessibility of the living ends.

A variation of these synthetic methods allowed the preparation of terminal hydroxy functional PMMA and α,ω-dihydroxy-PMMA. Ethyl 3-lithiopropyl acetaldehyde acetal[7] added to 1,1-diphenylethylene in THF at 0 °C to give the substituted diphenylmethyl anion **6** in quantitative yield. At −78 °C, **6** initiated polymerization of MMA with 100% efficiency to produce, after acid hydrolysis, hydroxy-PMMA **7** with n from 1 to 500 and $M_w/M_n < 1.2$. Similarly, the adduct of allyllithium and 1,1-diphenylethylene in place of **6** produced polymers like **4**. Living PMMA produced from **6** was coupled in 90% yield with 1,4-bis(bromomethyl)benzene and then hydrolyzed to give α,ω-dihydroxy-PMMA (**8**).



Methacrylate polymers 100% functionalized as in **7** and **8** have not been prepared before. We have used these materials to prepare PMMA with polymerizable functionality, block copolymers of PMMA with other polymer types (both AB and ABA types), and AAAA... block copolymers by chain extension of **8**.

Details of these and other related studies will be the subject of forthcoming publications.

References and Notes

(1) Braun, D.; Herner, M.; Johnsen, U.; Kern, W. *Makromol. Chem.* **1962**, *51*, 15.

(2) Fraenkel and Cooper (Fraenkel, G.; Cooper, J. C. *Tetrahedron Lett.* **1968**, 1825) showed by NMR that the *n*-butyllithium–pyridine adduct is the 2-alkyldihydropyridine amide. This was confirmed with phenyllithium by Giam and Stout (Giam, C. S.; Stout, J. L. *J. Chem. Soc., Chem. Commun.* **1969**, 142).

(3) (a) Wiles, D. M.; Bywater, S. *J. Polym. Sci., Part B* **1964**, *2*, 1175. (b) Wiles, D. M.; Bywater, S. *Trans. Faraday Soc.* **1965**, *61*, 150.

(4) Milkovich, R.; Chiang, M. T. (assignors to CPC International Corp.) U.S. Patent 3786116, Jan 15, 1974. This patent broadly discloses reactions of this type with vinylbenzyl chloride, but without experimental detail and without characterization. Vinylbenzyl *chloride* failed in our hands.

(5) Graham, R. K.; Panchak, J. R.; Kampf, M. J. *J. Polym. Sci.* **1960**, *44*, 411.

(6) Seow, P. K.; Lingelser, J.-P.; Gallot, Y. *Makromol. Chem.* **1977**, *178*, 107.

(7) Eaton, P. E.; Mueller, R. H.; Carlson, G. R.; Cullison, D. A.; Cooper, G. F.; Chou, T.-C.; Krebs, E.-P. *J. Am. Chem. Soc.* **1977**, *99*, 2751.

B. C. Anderson, G. D. Andrews,* P. Arthur, Jr.,
H. W. Jacobson, L. R. Melby,* A. J. Playtis, and
W. H. Sharkey

Contribution No. 2865 from
E. I. du Pont de Nemours and Company
Central Research and Development Department
Experimental Station, Wilmington, Delaware 19898

Received March 24, 1981

Polystyrene Fluorescence: Effects of Molecular Weight in Various Solvents

Intramolecular excimer formation is observed in dilute solutions of vinyl polymers containing aromatic groups. Hirayama[2] demonstrated in his study of di- and triphenylalkanes that intramolecular excimer formation occurs exclusively in chains in which the phenyl groups are separated by three carbon atoms. This "$n = 3$" rule also applies to adenine, carbazole, and naphthalene substituents.[3-5] Because excimer formation occurs by the rotation of bonds to bring two adjacent chromophores into a coplanar arrangement, the ratio of excimer to monomer fluorescence intensity (I_E/I_M) can be used as a probe of the conformational transitions in these molecules.

Polystyrene was one of the first polymers to be studied by fluorescence techniques.[6,7] From comparisons with model bibenzyl compounds, Vala et al.[8] concluded that the polystyrene fluorescence peak at 335 nm is due to excimer emission while the peak at 280–285 nm is due to monomer emission. A dramatic feature of polystyrene fluorescence is its molecular weight dependence. Not only is I_E/I_M higher for polystyrene than for low molecular weight model compounds containing several phenyl groups,[2,9] but there is also a difference in I_E/I_M for different molecular weights of polystyrene. Ishii et al.[10] have shown that I_E/I_M for dilute solutions of polystyrene in 1,2-dichloroethane (a good solvent for polystyrene) increases up to 1.0×10^4 daltons and is constant at higher molecular weights. The molecular weight effect is not confined to polystyrene; Aspler and Guillet[11] have shown a molecular weight dependence up to 3.6×10^5 daltons for the fluorescence of dilute solutions of poly(1-naphthyl methacrylate) in dichloromethane, and other studies have shown this effect in poly(α-vinylnaphthalene)[12] and poly(2-vinylnaphthalene).[13]

Copolymer studies have determined that excimer fluorescence decreases significantly when the aromatic component in the copolymer is less than 20 mol %[7,14] and that I_E/I_M is proportional to $f_{ss}\bar{l}_s$, where f_{ss} is the fraction of aromatic pairs in the copolymer and $\bar{l}_s$ is the mean sequence length of aromatics.[15] Energy migration was suggested as a possible explanation for this effect;[15] however, there remains some uncertainty about the role of singlet energy transfer.[16] Time-resolved fluorescence studies[17,18] have shown that excimer fluorescence increases with time after pulsing and that excimer dissociation to excited monomer can be observed in poly(1-vinylnaphthalene) but is unimportant in polystyrene solutions.

Spectroscopic quality cyclohexane, 1,2-dichloroethane, and ethyl acetate were used without further purification. Reagent grade decalin was purified by silica gel filtration. The polymer samples were standard polystyrenes with narrow molecular weight distribution (Pressure Chemical Co. and Polymer Laboratories) of molecular weight 725, 830, 2.0×10^3, 2.9×10^3, 9.0×10^3, 1.75×10^4, 2.5×10^4, 3.5×10^4, 5.0×10^4, 1.0×10^5, 2.0×10^5, 2.33×10^5, 6.0×10^5, 9.0×10^5, and 1.8×10^6. The head-to-head polystyrene was synthesized and kindly supplied to us by Dr. M. Malanga and Professor O. Vogl of the Department of Polymer Science and Engineering at the University of Massachusetts. According to their measurements, $[\eta] \simeq 0.7$ dL/g in tetrahydrofuran, which corresponds to a molecular weight of approximately 1.3×10^5. The concentration of polymer solutions was maintained at 5 mmol/L (chromophore unit) unless otherwise specified. I_E/I_M was independent of concentration near 5 mmol/L.

A mercury lamp was used as an excitation source. The exciting light (253.7 mm) was isolated by a chlorine gas filter and a Beckman DU spectrophotometer. The Suprasil sample cell had a 1-cm path length. A Beckman DU spectrophotometer was also used as the analyzing monochromator and was positioned at 180° to the excitation source. The slits on both spectrophotometers were maintained at 2 mm. The analyzed light was then processed through a photomultiplier and a Keithley 610C electrometer. Absorbance corrections to the fluorescence spectrum of the ethyl acetate solutions were made with a Cary 15 spectrophotometer.

All reported I_E/I_M measurements are for air-equilibrated solutions at 24 ± 1 °C unless stated otherwise, are un-

0024-9297/81/2214-1601$01.25/0