Synthesis of *p*-Methoxystyrene–Isobutyl Vinyl Ether Block Copolymers by Living Cationic Polymerization with Iodine

Toshinobu Higashimura,* Masakazu Mitsuhashi, and Mitsuo Sawamoto

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received November 21, 1978*

ABSTRACT: Optimum conditions for living cationic polymerization of *p*-methoxystyrene (pMOS) were established to allow a novel sequential block copolymer synthesis. Long-lived propagating species were obtained with iodine initiator at a low temperature (−15 °C) in a nonpolar solvent (CCl_4) or in a polar solvent (CH_2Cl_2) containing a common ion salt ((n-$C_4H_9)_4NI$), where the ionic dissociation of the growing end was suppressed. Under these conditions addition of isobutyl vinyl ether (IBVE) to a completely polymerized pMOS solution led to a new block copolymer, poly(pMOS-*b*-IBVE). Characterization of the block copolymer indicated that living poly(pMOS) in a nondissociated state is essential to effective block copolymerizations.

In the cationic polymerization of vinyl monomers, the low stability of propagating cations has prevented the formation of "living" polymers. However, we have recently found[1] that a long-lived propagating species can be obtained by use of a monomer and an initiator which form a stable cation and a highly nucleophilic counteranion, respectively. Thus we polymerized *p*-methoxystyrene (pMOS) with iodine initiator at 0 °C in tetrachloromethane (CCl_4). The long lifetime of the propagating species was indicated by the linear increase of polymer molecular weight with conversion and its further increase on addition of a new monomer feed when the first polymerization was completed.

In the following part of this paper, we use terms "living" and "long lived" in the equal sense, although a strict definition may require the complete absence of transfer and termination for "living" species, while "long-lived" species may undergo these reactions to some (but small) extent.

Our previous work[1] also suggested that the cationic polymerization of pMOS induced by iodine does not always generate living propagating species. Solvent polarity and polymerization temperature seem to have great influences on the lifetime of propagating cations. Therefore, this study first aims at clarifying optimum polymerization conditions. We polymerized pMOS by iodine at a lower temperature (−15 °C) than before in solvents of different polarities so that insight may be obtained into the mechanism of living cationic polymerization.

The second purpose of this study is synthesis of a new block copolymer through the living cationic polymerization. Two examples of the block copolymer synthesis by sequential cationic polymerization of vinyl monomers have so far been reported. Stannett et al.[2] block-copolymerized *N*-vinylcarbazol and vinyl ethers with a stable cationic salt which induces terminationless polymerizations, although frequent transfer reactions lowered the yield of copolymer. Pepper et al.[3] obtained block copolymers by polymerizing aziridines with dormant polystyryl perchlorate that could not react with styrene monomer. To our knowledge, however, no block copolymer of vinyl monomers has been prepared via well-defined living cationic polymerization. Based on our systematic study of the living polymerization of pMOS, we succeeded in the synthesis of a new block copolymer by the reaction of isobutyl vinyl ether (IBVE) with living poly(pMOS).

Experimental Section

Procedures. All polymerization processes were carried out in a dry nitrogen atmosphere. Polymerization of pMOS was initiated by injecting iodine solution to a monomer solution in a vessel attached to a three-way stopcock. In this procedure the polymerization system contains 0.2–0.3 mM water as impurity. After a certain interval, methanol containing a small amount of aqueous ammonia was added to terminate the reaction. Product polymers were precipitated in a large amount of methanol, filtered off, and vacuum dried. The conversion of pMOS was measured by gas chromatography with tetralin as internal standard.

Block copolymerization was carried out by adding an IBVE solution under dry nitrogen to a completely polymerized pMOS solution which was prepared as described above. After a certain interval, the reaction was terminated by methanol/aqueous ammonia and the conversion of IBVE was measured by gas chromatography with *n*-octane as internal standard.

Products were poured into a large amount of isopropyl alcohol (*i*-PrOH), extracted by stirring overnight, and fractionated into insoluble and soluble parts by filtration. Poly(IBVE) is soluble in *i*-PrOH and poly(pMOS) insoluble; separate experiments showed that a mixture of these homopolymers can be completely separated with *i*-PrOH into soluble (poly(IBVE)) and insoluble (poly(pMOS)) parts. The composition of pMOS-*b*-IBVE block copolymers (*i*-PrOH-insoluble part) was determined from the aliphatic to aromatic proton ratio measured by ^1H NMR (JOEL MH 60, in CCl_4). The molecular weight distribution (MWD) of polymers was obtained by gel permeation chromatography (GPC) on a Shimadzu Model GPC-700 in 2-butanone. Number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of polymers were calculated from GPC curves on the basis of a polystyrene calibration.

Materials. pMOS was synthesized from the corresponding acetophenone.[4] IBVE was commercially supplied and was distilled over calcium hydride before use. Iodine (Nakarai Chemicals, guaranteed reagent, purity >99.8%) and tetra-*n*-butylammonium iodide (n-Bu_4NI, Nakarai Chemicals, polarographic grade) were used without further purification. CCl_4 and dichloromethane (CH_2Cl_2) as solvents were purified by the usual methods and distilled over calcium hydride before use. Tetralin and *n*-octane (guaranteed reagents) were purified by distillation.

Results and Discussion

1. Optimum Conditions for Living Polymerization of pMOS.

Effect of Temperature. pMOS was polymerized in CCl_4 at a lower temperature (−15 °C) than that (0 °C) in the previous work.[1] "Monomer-addition" experiments were performed to examine the presence of living propagating species. In the presence of 10 mM iodine the initial feed of pMOS (0.50 M) was consumed completely within 6 h, and at this stage a second monomer feed (0.50 M) was added, which smoothly polymerized to 100% conversion within 20 h. Figure 1 shows the MWD of poly(pMOS) obtained before and after the monomer addition. The MWD curve shifted obviously toward higher molecular weight as the polymerization proceeded.

0024-9297/79/2212-0178$01.00/0

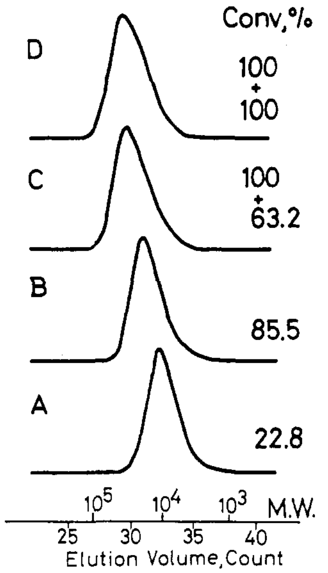


Figure 1. Effect of conversion on the MWD of poly(pMOS) obtained in CCl_4 at -15 °C before (A, B) and after (C, D) the monomer addition: $[I_2]_0$ = 10 mM. The initial monomer concentrations in the first and the second polymerizations were both 0.50 M. $\bar{M}_n$ (GPC): (A) 10900; (B) 12400; (C) 19800; (D) 22300.

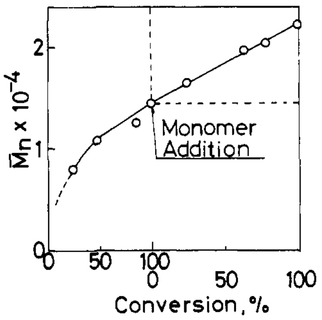


Figure 2. Relationship between $\bar{M}_n$ of poly(pMOS) and conversion before and after the monomer addition. Polymerization conditions are the same as in Figure 1.

Further, the monomer addition also caused a clear increase of molecular weight. It should be noted that the MWD curves shifted without broadening or tailing toward lower molecular weight and kept fairly low dispersities ($\bar{M}_w/\bar{M}_n \simeq 1.3$–$1.4$) at any conversion. Correspondingly, $\bar{M}_n$ increased almost linearly as the polymerization proceeded both before and after the monomer addition, as shown in Figure 2. These facts not only show the presence of living species but also suggest virtual absence of unreacted iodine at the end of the first polymerization; if a considerable amount of iodine had remained, it would have resulted in polymers of much lower molecular weights on monomer addition.

Under similar conditions pMOS was polymerized to a high conversion in the presence of a dead poly(pMOS). No change was found in the MWD of the poly(pMOS) after its recovery, which indicates that the observed increase of polymer molecular weight is by no means due to grafting of the propagating species onto dead poly(pMOS). Therefore, the results in Figures 1 and 2 show the presence of living propagating species in CCl_4 at -15 °C.

The number of polymer molecules (N) produced per unit initiator molecule can be calculated according to eq 1[1]

$$N = \frac{[M]_{\text{consumed}}}{\bar{P}_n} \times \frac{1}{[C]_0} \qquad (1)$$

where $\bar{P}_n$ is the number-average degree of polymerization (by GPC) and $[C]_0$ the initial concentration of iodine.

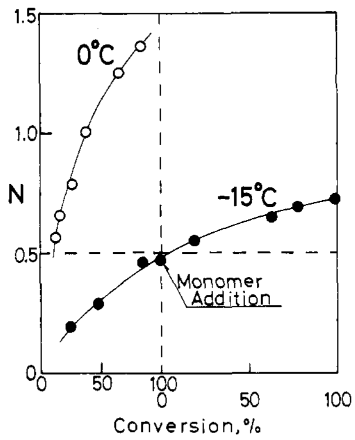
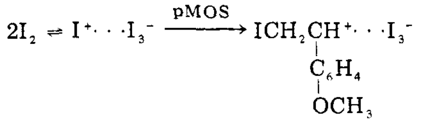


Figure 3. Relationship between the number of poly(pMOS) chains produced per unit initiator molecule (N) and conversion. Polymerization conditions at -15 °C are the same as Figure 1. Data for 0 °C are from ref 1.

Figure 3 shows the dependence of N on conversion in CCl_4 at -15 °C, together with the reported result at 0 °C at the same $[C]_0$.[1] At -15 °C N increased slightly with increasing conversion and approached 0.5 at the end of the first polymerization. After the monomer addition N finally reached about 0.7. At 0 °C, on the other hand, N already exceeded 1.0 at 50% conversion before the monomer addition and steeply increased with conversion.

Under the reasonable assumption of bimolecular initiation of iodine in CCl_4 (eq 2),[5]



$$2I_2 \rightleftharpoons I^{+}\cdots I_3^{-} \xrightarrow{\text{pMOS}} ICH_2\underset{\underset{OCH_3}{|}}{\underset{C_6H_4}{\underset{|}{C}}}H^{+}\cdots I_3^{-} \qquad (2)$$

a perfect living polymerization should result in N = 0.5 at any conversion. Therefore the N values obtained at -15 °C show that transfer is of less importance at lower temperatures and that the lifetime of the growing species is much longer than at 0 °C. The N values smaller than 0.5 in the early stage of the polymerization could be ascribed to a slow initiation, while those over 0.5 after the monomer addition might be caused by transfer reactions.

The above described results thus made it clear that lowering temperature in CCl_4 could lead to a living polymerization.

Effects of Solvent Polarity and Common Ion Salt. At 0 °C the polymerization of pMOS in CH_2Cl_2, a polar solvent, did not produce living propagating species in sharp contrast to the nearly living polymerization in CCl_4.[1] We therefore investigated whether living growing species could be produced in this polar solvent when polymerization temperature was lowered to -15 °C. Figure 4 depicts the MWD of poly(pMOS) obtained in CH_2Cl_2 at -15 °C before and after the monomer addition. The first-stage polymerization resulted in polymers with broader MWD ($\bar{M}_w/\bar{M}_n$ = 3.0–4.0) than those in CCl_4, as shown in Figure 4A, although $\bar{M}_n$ values slightly increased with conversion. Moreover, addition of a second pMOS feed did not cause an increase of polymer molecular weight but produced another lower molecular weight peak (Figure 4B,C). This may be ascribed to proton transfer from the growing end to added pMOS molecules. These results show that living polymerization cannot be realized in CH_2Cl_2 even at low temperatures.

The polymerization of pMOS by iodine is known to proceed via a nondissociated propagating species in CCl_4 and a dissociated species in CH_2Cl_2.[6] From the effect of

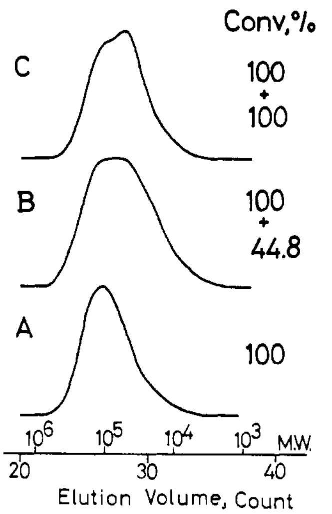


Figure 4. MWD of poly(pMOS) obtained in CH_2Cl_2 at −15 °C before (A) and after (B, C) the monomer addition: $[I_2]$ = 2.0 mM. The initial monomer concentrations in the first and the second polymerizations were both 0.50 M.

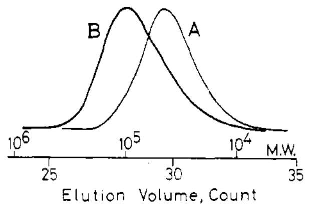


Figure 5. MWD of poly(pMOS) obtained in CH_2Cl_2 containing n-Bu_4NI at −15 °C before (A) and after (B) the monomer addition: $[I_2]_0$ = 3.3 mM; $[n\text{-}Bu_4NI]_0$ = 0.02 mM. The initial monomer concentrations in the first and the second polymerizations were both 0.50 M. $\bar{M}_n$ (GPC) and conversion: (A) 20600, 100%; (B) 31900, 100 + 91.4%.

solvent polarity described above, we speculated that formation of living poly(pMOS) requires suppressing the ionic dissociation of the propagating species. Then pMOS was polymerized in CH_2Cl_2 in the presence of a common ion salt. The first-stage polymerization produced low molecular weight polymers (Figure 5A), which corresponded to the polymers formed in CCl_4 (Figure 1) and much differed from those in salt-free CH_2Cl_2 (Figure 4A). Their MWD was fairly sharp ($\bar{M}_w/\bar{M}_n$ = 1.3) even at 100% conversion. Addition of a new pMOS feed to a completely polymerized solution clearly shifted the MWD curve to the higher molecular weight side (Figure 5B) as in CCl_4. This demonstrates that a long-lived propagating species is produced even in CH_2Cl_2 when the dissociation of the growing end is suppressed by a common ion salt.

Although the reasons why the resultant "nondissociated" species has a living nature are open to future investigations, the highly nucleophilic counterion (I_3^-), located in the close proximity of the stable growing end with strong interaction, may protect it from side reactions such as proton elimination.

2. Synthesis of Poly(*p*-methoxystyrene-*b*-isobutyl vinyl ether) Block Copolymer. The results described in the preceding section show the polymerization of pMOS can be "living" when suitable polymerization conditions are selected. The next subject of interest to us was synthesis of block copolymers through this living cationic polymerization. Thus IBVE as a second monomer was allowed to react with living poly(pMOS) under various conditions.

Block Copolymerization in CCl_4. Block Copolymerization of IBVE was first carried out in CCl_4 at −15 °C where living poly(pMOS) could be effectively prepared. A wine-red solution of completely polymerized pMOS ($[pMOS]_0$ = 0.50 M, $[C]_0$ = 10 mM) immediately turned colorless when a solution of IBVE in CCl_4 was added ($[IBVE]_0$ = 0.50 M). The added IBVE polymerized smoothly without showing an induction period. Polymerization products were fractionated into soluble and insoluble parts by extraction with *i*-PrOH (see Experimental Section). Figure 6 compares the ^{1}H-NMR spectrum of the *i*-PrOH-insoluble part with those for poly(IBVE), poly(pMOS), and their mixture. It resembled the spectrum of the homopolymer mixture, showing characteristic absorptions due to the isobutyl group (δ ca. 0.9 and 3.1). Because the insoluble part cannot contain homopoly(IBVE), this observation indicates clearly the production of block copolymers, although whether the insoluble part contains partly unblocked poly(pMOS) has not been made clear. In the *i*-PrOH-soluble part only homo-poly(IBVE) was extracted.

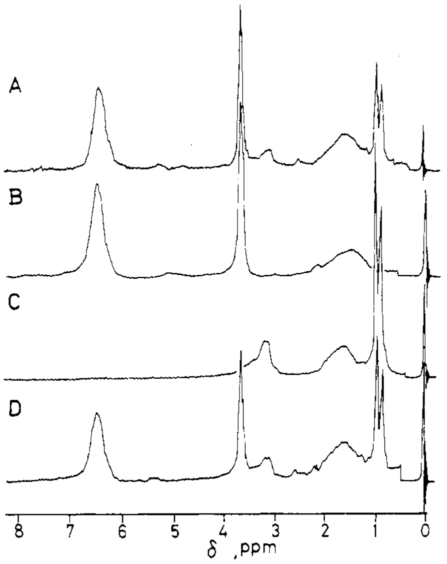


Figure 6. ^{1}H-NMR spectra of poly(pMOS-*b*-IBVE) block copolymer and relevant polymers obtained in CCl_4 at −15 °C: (A) block copolymer (sample No. 5 in Table I); (B) poly(pMOS) (sample No. 1 in Table I); (C) poly(IBVE); (D) mixture of poly(pMOS) and poly(IBVE) (10:3 w/w). The poly(IBVE) was prepared with iodine under similar conditions to those in the block copolymerization.

The block copolymer (insoluble part) had a higher molecular weight than the starting living poly(pMOS) (Figure 7) and byproduct poly(IBVE).

In a separate experiment IBVE was polymerized by iodine in the presence of a dead poly(pMOS) instead of a living poly(pMOS) under conditions similar to those in the block copolymerization. Extraction of the product at 80% IBVE conversion with *i*-PrOH gave an insoluble fraction which was confirmed by ^{1}H NMR and GPC to be identical to the dead poly(pMOS); no NMR absorption due to IBVE units was observed. This unambiguously excludes the possible grafting of propagating IBVE chains onto the aromatic rings of poly(pMOS), although cationic polymerization of styrene by $SnCl_4$ in the presence of a dead poly(pMOS) has been reported to yield graft copolymers.[7] The formation of a new block copolymer, poly(pMOS-*b*-IBVE), was thus confirmed.

Table I shows the results of characterization of the block copolymers obtained in CCl_4. (IBVE)/(pMOS) is the molar ratio of IBVE to pMOS in the block copolymer determined by ^{1}H NMR (see Experimental Section). This increased with increasing conversion. $\bar{M}_n$ of the block

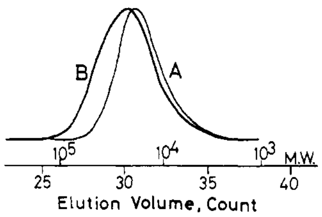


Figure 7. MWD of polymers before and after block copolymerization in CCl_4 at -15 °C: (A) starting living poly(pMOS) (sample No. 1 in Table I); (B) block copolymer (sample No. 5 in Table I).

Table I
Block Copolymerization of Isobutyl Vinyl Ether (IBVE) to Living Poly(*p*-methoxystyrene) in CCl_4 at -15 °C[a]

	sample no.				
	1	2	3	4	5
conv of IBVE, %	0	11.5	23.1	31.8	40.0
$\overline{M}_n \times 10^{-4}$[b]	1.27	1.33	1.39	1.47	1.68
(IBVE)/(pMOS)[c]	0	0.015	0.055	0.184	0.210
[P],[c] mM	5.3	5.1	5.0	5.2	4.6

[a] $[IBVE]_0 = 0.50$ M. Living poly(*p*-methoxystyrene) (sample No. 1) was prepared at $[I_2]_0 = 10$ mM and $[pMOS]_0 = 0.50$ M; pMOS conversion = 100 %. [b] Determined by GPC on the basis of a polystyrene calibration. [c] See text.

copolymer also increased almost linearly with increasing conversion (Figure 8). The number of block copolymer chains ([P], in mol/L) was calculated according to the following equation:

$$[P] = \frac{1}{\overline{M}_n}\left\{[pMOS]_0 \times 134 + [pMOS]_0 \times \frac{(IBVE)}{(pMOS)} \times 100\right\} \tag{3}$$

where $[pMOS]_0$ is the initial concentration of pMOS. The [P] value before IBVE addition corresponds to the concentration of living poly(pMOS) in the system and should be 5.0 mM at $[C]_0 = 10$ mM on assuming quantitative bimolecular initiation by iodine. Table I shows that this is the case with our system. The observed [P] values after IBVE addition still retained the value 5.0 mM, independent of the conversion of IBVE. This strongly suggests that living poly(pMOS) quantitatively initiated block copolymerization of IBVE, although the possibility could not necessarily be excluded that unblocked poly(pMOS) was partly contained in the *i*-PrOH-insoluble part. The blocking efficiency (BE), calculated by eq 4, was 39% at 32% IBVE conversion as shown in Table II.

$$BE = \frac{\text{molar amount of IBVE in block copolymer}}{\text{molar amount of IBVE consumed}} \tag{4}$$

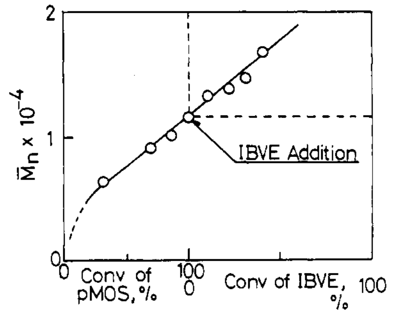


Figure 8. Relationship between $\overline{M}_n$ and monomer conversions before and after block copolymerization in CCl_4 at -15 °C: $[I_2]_0 = 10$ mM; $[pMOS]_0 = 0.50$ M; $[IBVE]_0 = 0.50$ M.

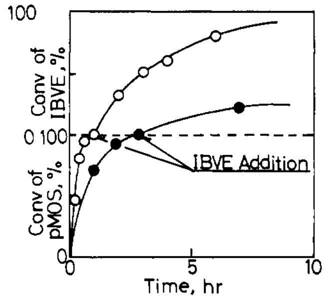


Figure 9. pMOS-*b*-IBVE block copolymerizations in CH_2Cl_2 at -15 °C in the presence and absence of a common ion salt (*n*-Bu_4NI): $[pMOS]_0 = 0.50$ M; (●) $[n\text{-}Bu_4NI]_0 = 0.02$ mM, $[I_2]_0 = 3.3$ mM, $[IBVE]_0 = 0.50$ M; (○) salt free, $[I_2]_0 = 2.0$ mM, $[IBVE]_0 = 1.0$ M.

These results strongly suggest that long-lived growing species are also involved in the second-stage polymerization of IBVE initiated by living poly(pMOS), although the value BE = 39% indicates the occurrence of the transfer reaction to some extent. Our recent work[8] has also presented evidence for long-lived propagating species of IBVE formed by iodine.

Block Copolymerization in CH_2Cl_2. In the previous section it was shown that living poly(pMOS) can be obtained in CH_2Cl_2 in the presence of a common ion salt but cannot be obtained in salt-free CH_2Cl_2. Block copolymerizations of IBVE in these two media were then examined and their time-courses are illustrated in Figure 9. In CH_2Cl_2 containing a small amount of *n*-Bu_4NI, the rate of IBVE consumption was smaller than in pure CH_2Cl_2 and nearly the same as that in CCl_4. The *i*-PrOH-insoluble parts obtained in the two systems showed ^{1}H-NMR absorptions characteristic of IBVE units, but the blocking efficiency was much higher in the salt-containing CH_2Cl_2 (27%) than in pure CH_2Cl_2 (4.2%) (Table II). Moreover, only in the former solvent did the MWD of polymers shift toward higher molecular weight on addition of IBVE. It was thus revealed that block copolymers could be produced in CH_2Cl_2 as effectively as in CCl_4 when a common ion salt was present to suppress the dissociation of the propagating species.

The block copolymerization method shown above is not fully satisfactory in view of its imperfect efficiency (maximum 39%) and the relatively short length of the IBVE block. Improving these limitations is now under

Table II
Effects of Solvent Polarity and Common Ion Salt (*n*-Bu_4NI) on Blocking Efficiency of IBVE to Living Poly(pMOS) ($[pMOS]_0 = 0.50$ M; -15 °C)

solvent	$[n\text{-}Bu_4NI]_0$, mM	$[I_2]_0$, mM	$[IBVE]_0$, M	conv of IBVE, %	blocking efficiency, %
CCl_4		10	0.50	31.8	39
CH_2Cl_2		2.0	1.0	32.1	4.2
CH_2Cl_2	0.02	3.3	0.50	20.3	27

investigation.

References and Notes

(1) T. Higashimura and O. Kishiro, *Polym. J.*, **9**, 87 (1977).
(2) J. M. Rooney, D. R. Squire, and V. T. Stannett, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1877 (1976).
(3) P. K. Bossaer, E. J. Goethals, P. J. Hackett, and D. C. Pepper, *Eur. Polym. J.*, **13**, 489 (1977).
(4) C. S. Marvel and G. L. Schertz, *J. Am. Chem. Soc.*, **65**, 2056 (1943); R. F. Nystram and W. G. Brown, *ibid.*, **69**, 1197 (1947).
(5) S. Okamura, N. Kanoh, and T. Higashimura, *Makromol. Chem.*, **47**, 19 (1961).
(6) T. Higashimura, O. Kishiro, and T. Takeda, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1089 (1976).
(7) H. C. Hass, P. M. Kamath, and N. W. Schular, *J. Polym. Sci.*, **24**, 25 (1957).
(8) T. Ohtori, Y. Hirokawa, and T. Higashimura, *Polym. J.*, in press.

Synthesis of a Nitro-Substituted Epoxy Resin from Distyryldinitrobenzene Derivatives

Sheng Yen Lee,* Seb Corbino, and Scot C. Chiang[1]

Department of the Army, Harry Diamond Laboratories, Adelphi, Maryland 20783.

Received January 21, 1977

ABSTRACT: A nitro-substituted epoxy resin, diglycidyl ether of 4,6-dinitro-1,3-bis(*p*-hydroxystyryl)benzene, has been synthesized and shown to be curable with an amine or an anhydride. The synthesis started with the condensation reaction of a dinitroxylene with a *p*-alkoxybenzaldehyde. The reaction proceeded readily on both methyl groups when the symmetrical 4,6-dinitro-*m*-xylene was used. The cleavage of the benzyl ether produced from the condensation with *p*-benzyloxybenzaldehyde was feasible, whereas the cleavage of the corresponding methyl ether was impractical. The bisphenol obtained appeared to be stable to oxidation. The products are probably of trans,trans configuration.

In our work on epoxy resins, we have taken an interest in the synthesis of a nitro-substituted epoxy resin by epoxidizing a bisphenol prepared from a distyrylbenzene derivative. An epoxy resin containing nitro group substituents could be used to formulate pyrotechnic binders. Also, some nitro epoxies are known to char heavily when burnt, and such charring propensity has been considered an important feature of an ablative material.[2,3] Reme reported in 1890 the condensation reaction of 2,4-dinitrotoluene with benzaldehyde.[4] Condensation of dinitroxylenes with substituted aldehydes may give distyrylbenzene derivatives which may be converted to the required bisphenol for epoxidation. The distyrylbenzene system has recently been a target of extensive investigation for its luminescence and laser-producing properties.[5-9] Many of these properties have been explored for use as scintillators[10,11] or patented as stabilizers for plastics.[12] With such interests, we describe in this paper our synthesis of a nitro-substituted epoxy resin and wish that this work may lead to the investigation of the optical properties of a series of distyrylbenzene compounds with various substitutents that can be derived from the nitro groups.

Experiment Section

Physical Methods. Infrared (IR) spectra were determined either in KBr pellets or on NaCl crystal plates with a Perkin-Elmer 467 grating IR spectrophotometer. Visible and ultraviolet (UV) absorption spectra were taken with a Cary 14 spectrometer. To obtain nuclear magnetic resonance spectra, either a Varian T-60 high-resolution NMR spectrometer or a JEOL FX-100 pulse FT spectrometer was used. The latter is equipped with a 5-mm variable temperature $^1H/^{13}C$ dual-frequency probe. For ^{13}C-NMR experiments, various irradiation modes were employed to obtain complete decoupling, off-resonance decoupling, and pulse-gated decoupling spectra. The number of scans varied between 2000 and 22000. The chemical shifts were measured relative to internal tetramethylsilane. Thermal analysis was conducted with a DuPont thermal analyzer 990 including both the differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA) modules. Melting point (mp) was determined by the capillary tube method and corrected. Elemental analysis was performed by the Galbraith Laboratories, Inc.

Materials. *p*-Hydroxybenzaldehyde and benzyl chloride were of ACS grade from Fisher Chemical; epichlorohydrin, ACS grade, from Pfaltz and Bauer, Inc.; *p*-anisaldehyde, practical grade, from Eastman Chemical; Nadic methyl anhydride (NMA), technical grade, from Allied Chemical; and 2,4-dinitro-*m*-xylene, practical grade, from Aldrich Chemical. 4,6-Dinitro-*m*-xylene was first prepared according to a known procedure[13,14] and later obtained from Aldrich Chemical (practical grade).

Condensation of 2,4-Dinitro-*m*-xylene with *p*-Anisaldehyde. A mixture of 1.96 g (10 mmol) of 2,4-dinitro-*m*-xylene (mp 84–5 °C, recrystallized from EtOH), 3.10 g (22.8 mmol) of *p*-anisaldehyde, and 10 drops of piperidine in a round-bottom flask was heated at 150 °C under reflux for 8 h with magnetic stirring. After the first and the 4th h of heating, the condenser was temporarily removed for a few minutes to evaporate the water produced in the condensation reaction. Ten more drops of piperidine were added each time to make up the loss in the evaporation periods. At the end of the reaction, the dark brown reaction mixture was poured into a beaker containing 100 mL of stirred ethanol. The alcoholic mixture was filtered. Concentration of the filtrate by vacuum evaporation gave a black slurry, the NMR spectrum of which indicated essentially a mixture of the unreacted starting materials. Purification of the alcohol-insoluble dark-brown solid (1.51 g) by elution chromatography with benzene over an alumina column yielded 1.29 g (41% yield) of 2,6-dinitro-5-(*p*-methoxystyryl)toluene (I), mp 154–5 °C. Recrystallization from benzene/hexane gave light orange needles: mp 155.8–166.8 °C; NMR ($CDCl_3$) δ 2.46 (s, 3, methyl), 3.85 (s, 3, methyoxy), 6.82 and 6.99 (s, 2, olefinic), 7.10–8.10 (m, 6, aromatic). Anal. Calcd for $C_{16}H_{14}N_2O_5$: C, 61.15; H, 4.49; N, 8.91. Found: C, 60.93; H, 4,53; N, 8.89.

Preparation of *p*-Benzyloxybenzaldehyde. A mixture of 244 g (2.0 mol) of *p*-hydroxybenzaldehyde, 265 g (2.1 mol) of benzyl chloride, 600 g (4.3 mol) of anhydrous potassium carbonate, and 1300 mL of anhydrous methyl ethyl ketone was heated under reflux for 10 h with mechanical stirring. The cooled reaction mixture was diluted with water and extracted with ether. The ether extracts were combined, washed with water and 10% NaOH solution, and dried over anhydrous K_2CO_3. Removal of the solvent by evaporation with a rotary evaporator under vacuum left an orange oil, which solidified rapidly. The solid was recrystallized from a minimum amount of ethanol to yield 292 g of *p*-benzyloxybenzaldehyde, mp 71–3 °C (lit.[15] mp 70 °C). An additional crop of 44 g, mp 70–4 °C, was obtained from the mother liquor (81% total yield): NMR ($CDCl_3$) δ 5.18 (s, 2, benzylic),