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End-Capping Analysis of Cationic Polymerization of Styrene Derivatives with Sodium β-Naphthoxide as Capping Agent. 1. Concentration and Chain-Length Distribution of the Propagating Species in Styrene Polymerization

Mitsuo Sawamoto, Akira Furukawa, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

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ABSTRACT: A new end-capping method, with sodium β-naphthoxide as capping agent, has been developed to determine the concentration ([P*]) and chain-length distribution of the propagating species in cationic polymerization of styrene. In the reactions initiated by acetyl perchlorate ($AcClO_4$) at 0 °C, the added naphthoxide combined quantitatively and instantaneously with the growing chains to form β-naphthoxy-capped polymers that exhibited a UV absorption of the end group at ca. 330 nm. On the basis of this band, [P*] and propagation rate constants (k_p) were determined; the initiation efficiency ($[P^*]/[AcClO_4]_0$) and the k_p values depended strongly not only on the polarity of polymerization solvents but on the initial monomer concentration. GPC analysis (UV at 330 nm), monitoring the naphthoxyl end group of the product polymers, provided the chain-length distribution of the propagating species. The distribution with CH_2Cl_2 or CH_2Cl_2/nitrobenzene mixed solvents showed two distinct populations (H* and L*), indicating the existence of two independent active species with different nature. H* and L* yielded the higher and the lower polymers, respectively, to result in a bimodal molecular weight distribution (MWD) of polystyrene. In less polar solvents (CH_2Cl_2/CCl_4 mixtures), the growing chains consisted of L* only, giving oligostyrenes with a unimodal MWD. Thus the great change of the MWD of dead polymers with solvent polarity, previously reported by the authors, has been accounted for in terms of the chain-length distribution of the active (propagating) species.

Introduction

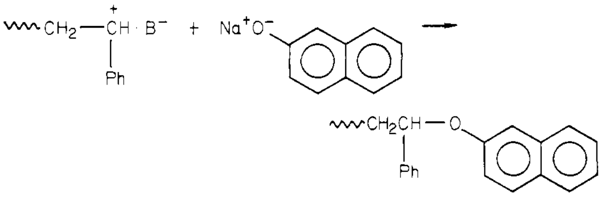
Determination of the concentration ([P*]) of the propagating species is of key importance in cationic polymerization for its quantitative understanding and control but is still the subject of active investigations. To this end two principal approaches, spectroscopic and chemical methods, have thus far been adopted.[1]

The spectroscopic methods mostly employ stopped-flow spectroscopy that can provide real-time electronic spectra of the propagating species, from which [P*] can be measured. Examples of its successful application are found in the polymerizations of styrene,[2–5] *p*-methoxystyrene,[6–9] and related monomers.[5,9] In spite of its high sensitivity and millisecond time resolution, suitable for analysis of short-lived species, stopped-flow spectroscopy has also disadvantages: Inherently, it cannot detect intermediates lacking a chromophore (e.g., aliphatic carbocations) and, moreover, a spectroscopically inactive ("invisible") propagating species exists even in *p*-methoxystyrene polymerization.[7,8]

The chemical or end-capping methods involve reaction of a basic capping agent with the growing species to introduce a detectable end group to the active chain. Such end-capping agents so far reported include 2-bromothiophene[10] for styrene polymerization and sodium phenoxide[11] and phosphines[12,13] for ring-opening polymerization of cyclic ethers and acetals. The former technique needs radioactivation analysis of 2-bromothiophene-capped polystyrene and, therefore, is not convenient and widely applicable. The end-capping using the latter two agents has been successful, but perhaps its application to vinyl-type cationic polymerization will encounter difficulties;[14] for instance, sodium phenoxide cannot be employed for styrene polymerization because of the overlapping UV absorptions of the phenoxyl end group and polystyrene.

The major advantages of the end-capping method over the spectroscopic technique are (1) that it is applicable to the spectroscopically nondetectable ("invisible") propagating species and (2) that in conjunction with GPC analysis of end-capped polymers, it can provide the chain-length distribution of the growing intermediates, which otherwise cannot be measured experimentally. The second advantage is particularly helpful to investigate the nature of the propagating species, especially its multiplicity in structure and reactivity now widely recognized in cationic polymerization.[7,8,16–18]

This paper presents a new end-capping method to determine [P*] and the chain-length distribution of the propagating species in cationic polymerization. We have selected sodium β-naphthoxide ($NaOC_{10}H_7$) as end-capping agent and critically examined its applicability to the polymerization of styrene initiated by acetyl perchlorate ($AcClO_4$). Under these conditions, the naphthoxide was found to combine quantitatively with the growing chains (eq 1) to form polystyrene with a β-naphthoxyl end group



(1)

that in turn serves as the probe for subsequent UV and GPC analyses. On the basis of the UV absorption of the β-naphthoxyl end group, [P*] and the propagation rate constant (k_p) were determined under a variety of conditions. GPC analysis of the end-capped polystyrene gave the chain-length distribution of the propagating species and thus provided direct evidence for the existence of two independent intermediates[16] in different dissociation states.

Experimental Section

Materials. $NaOC_{10}H_7$ was prepared from β-naphthol and sodium hydroxide by the method of Kornblum et al.[19] It was purified by three reprecipitations from methanol solution into benzene, followed by exhaustive washing with ether, and was dried in vacuo for 4–5 h at 100 °C and then for 2 days at room temperature. The final product, a slightly yellowish white fine powder, was sealed in ampules under dry nitrogen and stored in the dark. It showed a single GPC peak and was free from β-naphthol and other impurities according to NMR analysis (in Me_2SO-d_6).

(1-Bromoethyl)benzene and dimethylformamide (guaranteed reagents) were used as received. All materials for polymerization (styrene, $AcClO_4$, bromobenzene, nitrobenzene, CH_2Cl_2, and CCl_4)

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were obtained as reported previously.[16]

Polymerization Procedures. The polymerization of styrene by $AcClO_4$ was carried out at 0 °C under dry nitrogen; its details have been described.[16] At desired intervals, the reaction was quenched with $NaOC_{10}H_7$ (at least fivefold excess over the $AcClO_4$) suspended in CH_2Cl_2. Some runs were terminated with ammoniacal methanol. Styrene conversion was determined from its residual concentration by gas chromatography with bromobenzene as internal standard. The quenched reaction mixture was filtered and evaporated to dryness under reduced pressure at ca. 40 °C. The residue was dried under reduced pressure ($\sim$10 mmHg), dissolved in chloroform, and subjected to GPC analysis (see below). No oligomers were lost during the drying procedure.

Analysis of End-Capped Polystyrene. The purified polymers were analyzed by GPC with dual-mode [UV (330 nm) and refractive index (RI)] detection. GPC was run in chloroform eluent on a Jasco high-performance liquid chromatograph (TRIROTAR or FLC A-700) equipped with a polystyrene gel column (JSP 101, 21.5-mm i.d. × 500 mm, exclusion limit 3×10^3) and UV and RI detectors. UV spectra were recorded in CH_2Cl_2 on a Shimadzu UV-190 spectrophotometer.

Synthesis of (1-(β-Naphthoxy)ethyl)benzene.[19] A solution of (1-bromoethyl)benzene (>99 %) (2.7 mL, 20 mmol) in dimethylformamide (20 mL) was added dropwise to a stirred solution of $NaOC_{10}H_7$ (4.00 g, 24 mmol) in the same solvent (20 mL) at room temperature. After the addition was completed, the resulting mixture was stirred at room temperature for an additional 4–5 h and poured into 2% aqueous hydrochloric acid (100 mL). The product was extracted with benzene (100 mL), and the benzene extract was washed with Claisen potash [a potassium hydroxide (30 g) solution in a methanol (40 mL)/water (30 mL) mixture] and then water. Evaporation of the solvent followed by vacuum-drying at 60 °C gave (1-(β-naphthoxy)ethyl)benzene as a yellow-white solid in 70% yield: NMR ($CDCl_3$) δ 1.5 (3 H, d, CH_3), 5.2 (1 H, q, CH), 7.0–7.6 (12 H, m, aromatic H); UV (CH_2Cl_2) λ_{max} 329.5 nm. Anal. Calcd for $C_{18}H_{16}O$: C, 87.07; H, 6.50; O, 6.44. Found: C, 87.06; H, 6.57; O, 6.45.

Reaction of $NaOC_{10}H_7$ with $AcClO_4$. To a suspension of $NaOC_{10}H_7$ (0.092 g, 0.55 mmol) in CH_2Cl_2 (50 mL) was added a 64 mM solution of $AcClO_4$ (8.0 mL, 0.51 mmol) in CH_2Cl_2, with stirring at 0 °C. On addition of the $AcClO_4$ solution, the suspension became a transparent yellow-red solution. The resulting mixture was stirred for 1 min, washed with water, and evaporated to dryness to give 2-naphthyl acetate in a nealy quantitative yield: NMR ($CDCl_3$) δ 2.05 (3 H, s, CH_3), 7.0–7.9 (7 H, m, aromatic H); UV (CH_2Cl_2) λ_{max} 317 nm, $\epsilon = 3.16 \times 10^2$ M^{-1} cm^{-1}; IR (CCl_4) ν_{max} 1760 cm^{-1} (C=O), $\epsilon = 3.47 \times 10^3$ M^{-1} cm^{-1}.

Results and Discussion

Criteria for End-Capping with Sodium β-Naphthoxide. Successful determination of [P*] by an end-capping method requires the following:[10,11] (A) Quantitative and instantaneous termination of the polymerization by the capping agent, (B) complete removal of the unreacted terminating agent from end-capped polymers, (C) sensitive detection of the end group combined with the active center, and (D) absence of side reactions of the capping agent with the propagating species and/or dead polymers. These diagnostic criteria were examined in the end-capping using $NaOC_{10}H_7$.

On addition of the naphthoxide, the polymerization of styrene by $AcClO_4$ terminated immediately and completely (criterion A), although the quenching reaction was performed under heterogeneous conditions (see Experimental Section). Figure 1 shows this complete termination in the reaction in CH_2Cl_2 at 0 °C. In the absence of $NaOC_{10}H_7$, the polymerization took place smoothly up to high conversions within 40 min (open circles). When the capping agent was added at 20 min, on the other hand, the conversion remained unchanged afterward (filled circles).

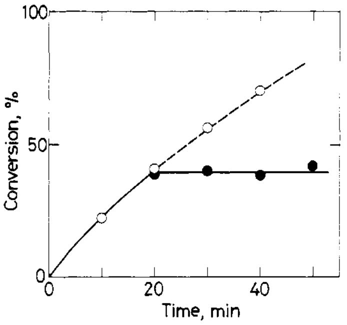


Figure 1. Polymerization of styrene by $AcClO_4$ at 0 °C in CH_2Cl_2: (●) quenched with $NaOC_{10}H_7$ at 20 min and further with methanol at the indicated time; (○) quenched with methanol only. $[M]_0 = 1.0$ M; $[C]_0 = 0.40$ mM.

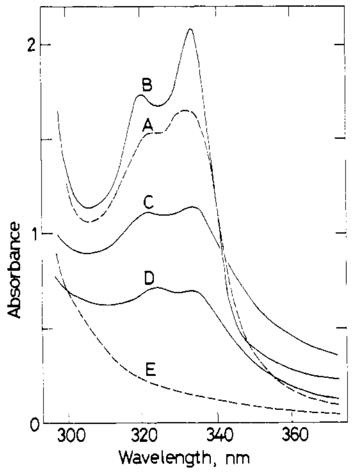
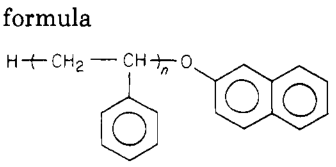


Figure 2. UV spectra in CH_2Cl_2: (A) β-naphthoxy-capped polystyrene; (B–D) β-naphthoxy-capped oligostyrenes I (B, dimer; C, trimer; D, tetramer); (E) polystyrene quenched with methanol. Samples A and E were obtained in the styrene polymerization by $AcClO_4$ at 0 °C in a CH_2Cl_2/CCl_4 mixture (2/1 (v/v)) ($[M]_0 = 0.25$ M; $[C]_0 = 2.0$ mM; see Figure 4b); samples B–D were separated from product A by GPC.

The polymers recovered after quenching with $NaOC_{10}H_7$ were purified by preparative GPC. The unreacted quencher elutes much later than oligostyrenes so that it can readily be removed from the products (criterion B). Preparative GPC also enabled separation of β-naphthyl acetate, another contaminant resulting from the reaction of the naphthoxide with the remaining $AcClO_4$ (see below).

The end-capped polymers thus purified exhibited a characteristic absorption at ca. 330 nm (Figure 2A). Such an absorption is absent in the spectrum of methanol-quenched polystyrene ($\bar{M}_n \sim 10^3$), which shows only a flat background band of styryl units in the region above 320 nm (Figure 2E). The resemblance in shape and position between the absorption at 330 nm and that of (1-(β-naphthoxy)ethyl)benzene (λ_{max} 330 nm) indicates the presence of a β-naphthoxyl group at the polymer chain end. According to GPC analysis (polystyrene calibration), the molecular weights of oligostyrenes in the end-capped products fitted in with a series of the calculated values based on the formula



I, $n = 1, 2, \ldots$

Each of the oligomer fractions, separated by GPC, showed an absorption of the β naphthoxyl end group (Figure 2B–D); for example, the following were obtained [λ_{max} in nm (ϵ_{max} in M^{-1} cm^{-1})]: $n = 1$, 330 (1830); $n = 2$, 336 (2550); $n = 3$, 335 (3160); $n = 4$, 333 (3160). The lowest oligomer

Table I
Concentrations of the Propagating Species ([P*]) and the Unreacted Initiator ($[AcClO_4]_f$) in the Polymerization of Styrene by $AcClO_4$ in CH_2Cl_2 at 0 °C

$[M]_0$, M	$[C]_0$, mM	[P*],[a] mM	$[AcClO_4]_f$, mM	[P*] + $[AcClO_4]_f$, mM
0.050	2.0	0.469	1.34	1.81
0.25	2.0	0.810	1.07	1.88
1.0	0.50	0.496	0.00	0.496

[a] Independent of monomer conversion.

fraction gave ^1H NMR and UV spectra identical with those of an authentic sample of (1-(β-naphthoxy)ethyl)benzene, i.e., the β-naphthoxy-capped monomeric propagating species (I, $n = 1$). Therefore, we concluded that the end-capping with $NaOC_{10}H_7$ yields β-naphthoxy-capped polystyrenes I *and that their terminal group can readily be detected by UV spectroscopy* (criterion C).

Quantitative UV analysis showed that the molar absorption coefficients at 330 nm of I with n = 1–4 (see above) fall in the narrow range $(1.83 \pm 0.15) \times 10^3$ M^{-1} cm^{-1} after correction for the spectral background due to the styryl units. The background correction was made by subtracting the spectrum of methanol-quenched polystyrene ($\bar{M}_n \sim 10^3$) from those of compounds I (n = 1–4), all the spectra being normalized to wavelengths above 370 nm, where no absorptions of the β-naphthoxyl end-group exist (see Figure 2). The corrected ε value was then employed as the molar absorption coefficient for β-naphthoxy-capped polystyrene in subsequent [P*] determination.

Absence of Side Reactions. This section describes experimental data showing the fulfillment of criterion D.

The polymerization of styrene initiated by $AcClO_4$ at 0 °C in CH_2Cl_2 follows a stationary-state kinetics[16] and gives a linear first-order plot for monomer consumption (Figure 3). The polystyrene samples, obtained after quenching with $NaOC_{10}H_7$, exhibited an absorption at ca. 330 nm due to the β-naphthoxyl terminal (Figure 2A). The [P*] values based on this band are independent of monomer conversion (Figure 3). The constancy of the observed [P*] values throughout the polymerization is consistent with the linear first-order plot.

In the course of this study, we found that $NaOC_{10}H_7$ reacts quantitatively with $AcClO_4$ to give β-naphthyl acetate (see Experimental Section). Therefore, when added to a polymerization solution initiated by $AcClO_4$, $NaOC_{10}H_7$ combines not only with the propagating species but with unreacted initiator, if present. The acetate has characteristic UV (317 nm) and IR (1760 cm^{-1}) absorptions, so that its concentration can be measured spectroscopically. The acetate quantity in turn represents the concentration of the free initiator, $[AcClO_4]_f$, remaining in the solution.

Table I lists typical $[AcClO_4]_f$ and [P*] values, both of which were determined independently. The combined concentration of the unreacted $AcClO_4$ and the propagating species ($[AcClO_4]_f$ + [P*]) is close to the initial initiator concentration ($[C]_0$). This demonstrates clean, quantitative addition of $NaOC_{10}H_7$ to the growing center and hence the validity of the [P*] values obtained by the end-capping method.

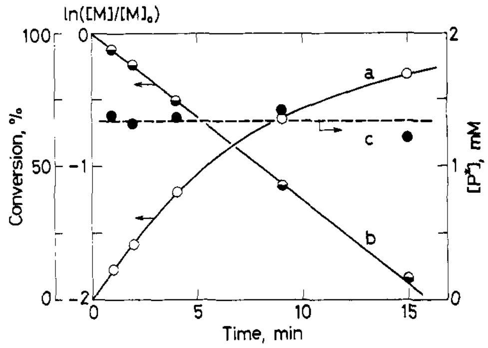


Figure 3. Kinetic profiles of the styrene polymerization by $AcClO_4$ at 0 °C in CH_2Cl_2: (a) monomer conversion, (b) ln ($[M]/[M]_0$), and (c) [P*] as functions of time. $[M]_0$ = 0.50 M; $[C]_0$ = 2.0 mM.

The most probable side reaction induced by $NaOC_{10}H_7$ is β-proton elimination from the propagating species, which leads to poly- or oligostyrene with terminal unsaturation (~~~-CH=CHPh). If this reaction took place, [P*] values based on the UV absorption of the terminal β-naphthoxyl group would be smaller than the actual [P*], or $[AcClO_4]_f$ + [P*] < $[C]_0$. The data shown in Table I exclude such underestimation of [P*] due to the deprotonation of the growing species promoted by added $NaOC_{10}H_7$. Criterion D was thus satisfied.

[P*] and k_p Values. Effects of Solvent Polarity and Monomer Concentration. [P*] and k_p values were then determined by the end-capping method using $NaOC_{10}H_7$ in the polymerizations in three solvents of different polarity. Table II lists representative results.

In all solvents, the polymerization immediately stopped on addition of the naphthoxide, and the [P*] values remained unchanged during the reaction (cf. Figure 3). Correspondingly, first-order plots for monomer consumption were linear; k_p values were obtained from the slope of the plots and the stationary-state concentration of the propagating species.

The first three lines of Table II show the effect of solvent polarity on [P*] and k_p at the same monomer concentration ($[M]_0$). While the initiation efficiency ($[P^*]/[C]_0$) was nearly the same in the three solvents, k_p increased remakably with solvent polarity. This suggests a great change in the nature of the propagating species along with solvent polarity (see below).

Another important finding is the clear dependence of [P*] and k_p on $[M]_0$ in the solvents having the same dielectric constant (last four lines, Table II). With decreasing $[M]_0$, the initiation efficiency decreased whereas k_p in-

Table II
[P*] and k_p Values in the Styrene Polymerization by $AcClO_4$ at 0 °C

solvent	DC[a]	$[M]_0$, M	$[C]_0$, mM	[P*],[d] mM	$[P^*]/[C]_0$, %	k_p, M^{-1} s^{-1}
CH_2Cl_2/CCl_4	6.40[b]	0.50	2.0	1.16	58	0.28
CH_2Cl_2	8.38	0.50	2.0	1.36	68	1.49
$CH_2Cl_2/C_6H_5NO_2$	10.70	0.50	0.40	0.25	63	9.64
$CH_2Cl_2/C_6H_5NO_2$	10.70[c]	0.25	0.40	0.19	47	17.1
$CH_2Cl_2/C_6H_5NO_2$	10.70	0.10	0.40	0.18	45	22.2
$CH_2Cl_2/C_6H_5NO_2$	10.70	0.05	0.40	0.14	35	36.0

[a] Dielectric constant of the polymerization solution calculated as the volume average of those of solvent(s), styrene, and bromobenzene (internal standard for gas chromatography). [b] 2/1 (v/v) CH_2Cl_2/CCl_4. [c] 7/1 (v/v) $CH_2Cl_2/C_6H_5NO_2$.
[d] Independent of monomer conversion.

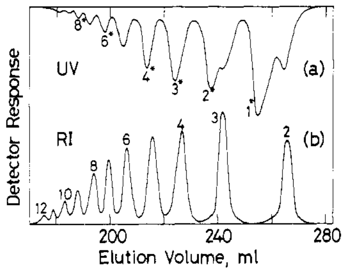


Figure 4. Chain-length distributions of the propagating species (a) and dead polymers (b) in the polymerization of styrene by $AcClO_4$ at 0 °C in a CH_2Cl_2/CCl_4 mixture (2/1 (v/v)): $[M]_0 = 0.25$ M; $[C]_0 = 2.0$ mM; conversion 40%.

creased; at $[M]_0 = 2.0$ M or above, $[P^*]/[C]_0$ reached 100% (data not shown). Chmelir has reported, similarly, that the overall polymerization rate increased at lower $[M]_0$ in the styrene/CF_3SO_3H system.[20]

The k_p values determined by our end-capping method are much smaller than those by stopped-flow spectroscopy ($\geq 10^4$ M^{-1} s^{-1}).[2-5] It should, however, be pointed out that the spectroscopic k_p measurements are always performed at very low $[M]_0$ ($\sim 10^{-3}$ M). The progressive increase in k_p with decreasing $[M]_0$ seen in Table II suggests that the reactivity of the propagating species is affected not only by solvent polarity but by monomer concentration as well. In fact, our preliminary end-capping analysis on polymerizations at very low $[M]_0$ ($\sim 10^{-3}$ M)[5] did give large k_p, of the order of 10^4 M^{-1} s^{-1}. The reason(s) for the great effects of monomer concentration is now being investigated in our laboratory.

Chain-Length Distribution of Propagating Species. Figure 4 shows the dual-mode (UV and RI) GPC traces for the polystyrenes obtained after end-capping with $NaOC_{10}H_7$ in a typical experiment. The products consist of oligomers because the polymerization solvent was a CH_2Cl_2/CCl_4 mixture (2/1 (v/v)) of low polarity.[16]

UV detection at 330 nm responds to only β-naphthoxy-capped polymers, and each UV peak indicates the relative concentration of the propagating species with a certain chain length. Therefore, the UV trace for an end-capping product represents the chain-length distribution of the propagating species. According to a polystyrene calibration, all UV peaks in Figure 4 correspond to β-naphthoxy-capped polystyrenes up to octamer (I, n = 1–8); e.g., peaks 1* and 3* are assigned to the monomeric and the trimeric propagating species, respectively. The observed distribution curve shows that the concentration of each growing species decreases monotonously with increasing degree of polymerization. The shoulders of peaks 1* and 2* are due to the overlapping styrene dimer and trimer having an unsaturated terminal (see below).

The RI trace shows the chain-length (or conventionally, molecular weight) distribution of the total products, virtually all of which are "dead" polymers formed through chain-transfer reaction(s). On the basis of NMR and IR analyses, the major fractions, separated by GPC, were identified as oligostyrenes with a terminal double bond (~~~–CH=CHPh).

Thus the dual-mode GPC analysis of the polymers obtained after quenching with $NaOC_{10}H_7$ provides the chain-length distributions of both the active propagating species and dead polymers. To our knowledge, the chain-length distribution of the growing species has been obtained experimentally for the first time in cationic polymerization.

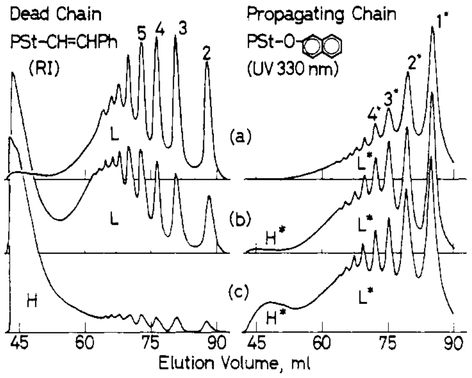


Figure 5. Chain-length distributions of the propagating species (right) and dead polymers (left) in the styrene polymerization by $AcClO_4$ at 0 °C: $[M]_0 = 0.25$ M; $[C]_0 = 1.1$ (b and c) or 2.0 (a) mM; conversion 10–40%. Solvent (v/v): (a) CH_2Cl_2/CCl_4 (2/1); (b) CH_2Cl_2; (c) $CH_2Cl_2/C_6H_5NO_2$ (7/1). Numbers indicate the degree of polymerization.

Effect of Solvent Polarity on Chain-Length Distributions. Figure 5 compares the chain-length distributions of the propagating species and the MWD of dead polymers obtained in three solvents.

The propagating species present in CH_2Cl_2 (b) or a $CH_2Cl_2/C_6H_5NO_2$ mixture (c) (7/1 (v/v)) consist of two components, H* and L*, with different chain lengths and chain-length distributions. The polymeric species (H*) increase in polar solvents (c > b), whereas only the oligomeric intermediates (L*) exist in a less polar medium (a) (CH_2Cl_2/CCl_4, 2/1 (v/v)). The bimodal chain-length distributions thus provided conclusive evidence for the existence of the two independent propagating species proposed previously on the basis of the MWD of dead polymers (see below).[16]

The dead polymers formed in CH_2Cl_2 exhibit a bimodal MWD. We have already confirmed that such an unusual MWD is not due to side reactions with adventitious impurities but results from the multiple propagating species.[16] The higher polymer peak[21] of the bimodal MWD decreased with decreasing solvent polarity, and only an oligomeric population was observed in the CH_2Cl_2/CCl_4 mixture. Thus, the chain-length distribution of the dead polymers changes in accordance with that of the propagating species; the close correlation between the two distributions shows that the polymeric species H* give the higher polymers while the oligomeric species L* form the lower polymers.

Comparison of the RI and UV traces (e.g., Figure 5b) shows that a small quantity of H* leads to a large amount of the higher polymers. In a polar solvent ($CH_2Cl_2/C_6H_5NO_2$ (7/1) mixture), the majority of dead polymers belongs to the higher polymer peak, whereas the oligomeric active species L* predominates over H*. These facts indicate a greater reactivity of H* that, if present, consumes most of the monomer feed. The k_p for L* may be $\sim 10^{-1}$ M^{-1} s^{-1} (CH_2Cl_2/CCl_4 solvent, Table II), whereas that for H* may be 10 M^{-1} s^{-1} or greater ($CH_2Cl_2/C_6H_5NO_2$ mixtures, Table II); thus H* will be 2 orders of magnitude more reactive than L*.

Registry No. Styrene, 100-42-5; $AcClO_4$, 2889-74-9; $NaOC_{10}H_7$, 875-83-2.

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New Poly[bis(benzimidazobenzisoquinolinones)]

Z. J. Jedliński,* B. Kowalski, and U. Gaik

Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland.
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ABSTRACT: A series of new poly[bis(benzimidazobenzisoquinolinones)] has been obtained by the condensation of 4,4′-oxydinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1a**), 4,4′-(phenylene-1,3-dioxy)dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1b**), 4,4′-(sulfonylbis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1c**), and 4,4′-(isopropylidenebis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1d**) with aromatic tetraamines. The polycondensations were carried out at high temperature in *m*-cresol containing benzoic acid. The polymers are soluble in *m*-cresol and phenol–chlorinated hydrocarbon mixtures. Tough, flexible films can be cast from dilute solutions. The polymers are amorphous and show good thermal and oxidative stability.

Introduction

Poly[bis(benzimidazobenzophenanthrolines)] belong to a group of ladder heterocyclic polymers exhibiting high thermal stability and good chemical resistance. The first polymers of this type were obtained by Van Deusen[1-3] from the polycondensation of 1,8:4,5-naphthalenetetracarboxylic dianhydride with aromatic tetraamines. These polymers showed high softening temperatures and were soluble only in strong acids (polyphosphoric acid, concentrated H_2SO_4, and methanesulfonic acid), which severely restricted their applications. Subsequent investigations on the chemical modification of poly[bis(benzimidazobenzophenanthrolines)] involved the insertion of dioxyarylene, dioxydiarylene,[4] or hexafluoropropylidene[5] linkages between the rigid aromatic–heterocyclic condensed units of the polymer chain. As a result, polymers soluble in organic solvents (*m*-cresol and phenol–chlorinated hydrocarbon mixtures) with glass transition temperatures below their respective decomposition temperatures were obtained. The flexible linkages were introduced into the polymer chain by the use of suitable tetraamine monomers. However, the methods of preparing such monomers are very cumbersome and expensive, which severely restricts the applications of these polymers.

The aim of our investigations was the preparation of fusible and soluble poly[bis(benzimidazobenzisoquinolinones)], which also belong to the poly[bis(benzimidazobenzophenanthroline)] class of ladder polymers. The monomers selected for their preparation were commercial aromatic tetraamines and dinaphthalene-derived dianhydrides, obtained from acenaphthene.

Experimental Section

Monomers. 3,3′-Diaminobenzidine (2a). This commercially available reactant was purified by recrystallization from deoxygenated water under an inert atmosphere, mp 177–179 °C (lit.[6] mp 178–179 °C).

3,3′,4,4′-Tetraaminodiphenyl ether (2b) was obtained by the procedure described in ref 7, mp 150–151 °C (lit.[8] mp 149–151 °C).

Bis(3,4-diaminophenyl)methane (2c) was prepared as previously described,[8] mp 139–140 °C (lit.[8] mp 137–138 °C).

4,4′-Oxydinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (1a) was prepared from acenaphthene according to the scheme given in ref 9. A solution of 4.3 g (0.025 mol) of 5-hydroxyacenaphthene, obtained as described in ref 10–12, and 0.1 g (0.0005 mol) of *p*-toluenesulfonic acid in 13 mL of 1,2,4-trichlorobenzene was heated for 35 h at 185 °C in an inert atmosphere. The solvent was removed by distillation. The residue was dissolved in 150 mL of benzene and extracted with 1 N NaOH to remove unreacted 5-hydroxyacenaphthene. After evaporation of the solvent, the crude product was purified by chromatography on silica gel (Kieselgel 100, 70–230 mesh) with a 9:1 hexane–benzene mixture as the eluent, yielding 2.3 g (56.7%) of white crystalline 5,5′-oxydiacenaphthene (mp 149 °C): IR (Nujol) ν_{C-O-C} 1250, $\nu_{C=C}$ 1590 cm^{-1}; molecular mass in mass spectrum, *m/e* 322. Anal. Calcd for $C_{24}H_{18}O$ (322.43) C, 89.4; H, 5.6. Found: C, 89.2; H, 5.3.

A solution of 2.0 g (0.006 mol) of 5,5′-oxydiacenaphthene and 16.4 g (0.06 mol) of sodium dichromate in 150 mL of glacial acetic acid was refluxed for 6 h. The reaction mixture was then poured into 200 mL of water. The precipitate that formed was collected by filtration and dissolved in 500 mL of 20% Na_2CO_3. The solution was filtered and acidified to afford a crude product. Crystallization from dimethylformamide (DMF) yielded 1.6 g (63%) of the yellowish final product **1a**: mp 356 °C dec; IR (Nujol) $\nu_{C=O}$ 1730, 1770, ν_{C-O-C} 1250, $\nu_{C=C}$ 1595 cm^{-1}; molecular mass in mass spectrum, *m/e* 410. Anal. Calcd for $C_{24}H_{10}O_7$ (410.36): C, 70.2; H, 2.5. Found: C, 69.9; H, 2.3.

4,4′-(Phenylene-1,3-dioxy)dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (1b) was prepared by the published procedure [13] with several modifications. To a stirred solution of 29.09 g (0.105 mol) of 4-bromo-1,8-naphthalic anhydride in 250 mL of dimethylformamide under nitrogen at 70 °C was added 7.70 g (0.05 mol) of the disodium salt of resorcinol over 0.5 h. The mixture was heated to 140 °C and maintained at that temperature for 8 h. After cooling, the solution was poured into water (~500

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