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Stopped-Flow Study of the Cationic Polymerization of Styrene Derivatives. 1. Direct Observation of the Propagating Species in the Polymerization of *p*-Methoxystyrene in 1,2-Dichloroethane

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ABSTRACT: Stopped-flow spectroscopy allowed the direct observation of the propagating species in the cationic polymerization of *p*-methoxystyrene in 1,2-dichloroethane at 30 °C. The reactions with four initiators (iodine, CH_3SO_3H, $BF_3O(C_2H_5)_2$, and $SnCl_4$) gave almost identical absorption spectra centered at 380 nm, which were assigned to the propagating carbocation. The absorbance changes at 380 nm showed a quantitative correlation with monomer consumption rate (monitored at 295 nm) to give propagation rate constants (k_p). The k_p values for the four initiator systems ranged from 4×10^3 to 2×10^4 $M^{-1}\ s^{-1}$ and were practically independent of the initiators, indicating that the nature of the observed propagating species does not depend on counterions. On the other hand, the maximal concentration ($[P^*]_{max}$) of the propagating species strongly depended on the initiators; i.e., with the metal halides $[P^*]_{max}$ was 5–25% of the initiator concentration ($[C]_0$), whereas iodine and CH_3SO_3H gave much smaller $[P^*]_{max}$ (ca. 0.1% of $[C]_0$).

The chemistry of the propagating species is one of the most important but still unsolved problems in the cationic polymerization of vinyl compounds. In most studies this has been discussed in an indirect manner based on overall polymerization kinetics and the structure of product polymers. Our recent work also deals with the rate and molecular weight distribution of polymers in styrene polymerization.[1] Direct and quantitative information on the propagating species may be given by its spectroscopic observation.

Stopped-flow spectroscopy allows the sensitive detection of transient reaction intermediates with a millisecond time resolution.[2] Pepper and his co-workers[3,4] recently applied this technique to the cationic polymerization of styrene by perchloric acid in dichloromethane at low temperatures. They detected a transient absorption at 340 nm, which was assigned to the polystyrylcarbenium ion. Kunitake and Takarabe[5] have also reported the observation of carbocationic intermediates in several systems. In spite of these results, however, there is a substantial lack of information on the propagating species.

This first paper of our series describes a stopped-flow study of the cationic polymerization of *p*-methoxystyrene by a variety of initiators in 1,2-dichloroethane. We have chosen the monomer because it is reactive in polymerization and should form a relatively stable carbocation that is suitable for spectroscopic observation. With four initiators (iodine, CH_3SO_3H, $BF_3O(C_2H_5)_2$, and $SnCl_4$), we found a common intermediate absorption to be due to the propagating species. This led to the determination of its concentration and propagation rate constant discussed below.

Experimental Section

Materials. *p*-Methoxystyrene was prepared from *p*-methoxyacetophenone by the reduction with $LiAlH_4$ followed by the dehydration of the corresponding alcohol with $KHSO_4$.[6] Distillation over calcium hydride under reduced pressure gave a monomer with a gas-chromatographic purity better than 99%. Iodine (Nakarai Chemicals, purity ≥99.8%) was used as received without further purification. Methanesulfonic acid (CH_3SO_3H), boron trifluoride etherate ($BF_3O(C_2H_5)_2$), and stannic chloride ($SnCl_4$) were purified by distillation of commercial products. 1,2-Dichloroethane as solvent

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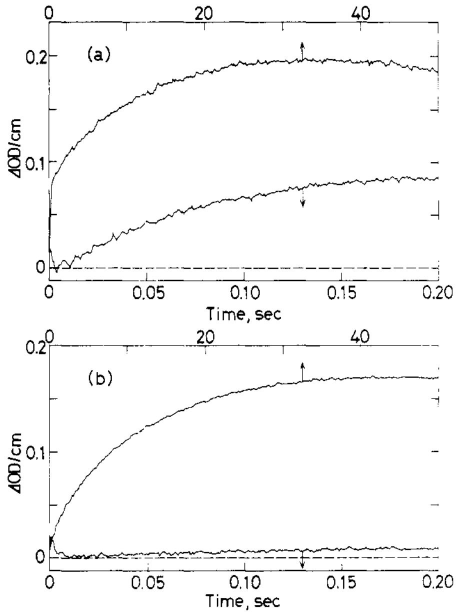

Figure 1. Typical recorder traces for the p-methoxystyrene/iodine system in 1,2-dichloroethane at 30 °C: (a) at 320 nm; (b) at 380 nm. $[M]_0$ = 5.0 mM; $[C]_0$ = 5.0 mM.

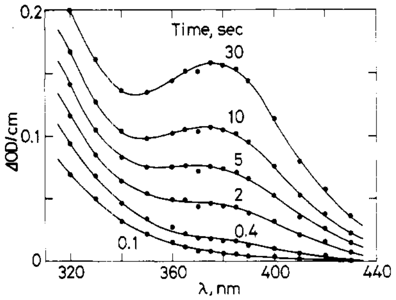

Figure 2. Time-resolved absorption spectra of the p-methoxystyrene/iodine system in 1,2-dichloroethane at 30 °C: $[M]_0$ = 5.0 mM; $[C]_0$ = 5.0 mM.

was washed with 10% aqueous sodium hydroxide solution and then water, was dried overnight with calcium chloride, and was distilled successively over phosphorus pentaoxide and calcium hydride just before use.

Procedures. Spectroscopic measurements were performed on a stopped-flow apparatus (RA-401; Union Giken) in 1,2-dichloroethane at 30 °C. Prior to measurements, the flow system was thoroughly washed with dry solvent and was flushed with dry nitrogen for more than 10 min. Monomer and initiator solutions, prepared under dry nitrogen, were then introduced to the reservoirs with hypodermic syringes against a dry nitrogen stream through specially designed stoppers. Reactions were initiated by driving the two solutions directly with pressurized (ca. 5 atm) dry nitrogen into the thermostated mixer and observation cell. The water concentration in the reaction mixture was 0.7–0.9 mM (by the Karl-Fischer method) at the outlet of the flow system, and hence that in the cell must be below this range. Output absorbance readings were accumulated up to five times by using a data processor to improve the signal-to-noise ratio.

Results and Discussion

Polymerization by Iodine. The reaction of p-methoxystyrene ($[M]_0$ = 5.0 mM) with iodine ($[C]_0$ = 2.5–15 mM) was followed spectrophotometrically in 1,2-dichloroethane at 30 °C. Figure 1 represents typical recorder traces showing absorbance changes at 320 and 380 nm. Time-resolved absorption spectra of the reaction mixture (Figure 2) were constructed from these traces by point mapping. Just after mixing the monomer and iodine, an absorption with a maximum at 320 nm or below was observed and, more slowly, another peak appeared at about 380 nm. Similar spectra were obtained at other iodine concentrations than those in Figure 2.

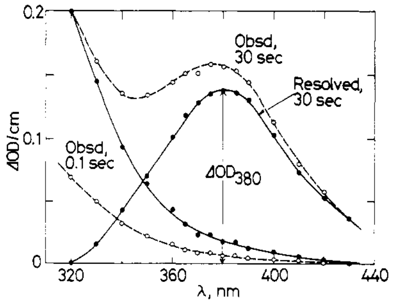

Figure 3. Example of resolution of the spectra shown in Figure 2 (t = 30 s).

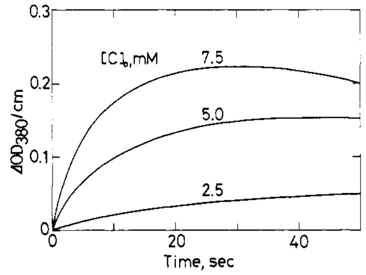

Figure 4. Absorbance changes at 380 nm in the p-methoxystyrene/iodine system in 1,2-dichloroethane at 30 °C: $[M]_0$ = 5.0 mM.

Since the 380-nm band was hardly detected at the early stage of the reaction (e.g., at 0.1 s; see Figure 2), this band was separated from the short-wavelength band by subtracting the spectrum at 0.1 s, normalized to 320 nm, from a composite spectrum at a given time. Figure 3 shows an example of this resolution (at 30 s), which led to a band centered at 380 nm. The absorbance at 380 nm (ΔOD_{380}) after the resolution was accurately proportional to those at any wavelengths from 320 to 450 nm, so that the extracted peak must be due to a single chemical species.

ΔOD_{380} thus determined was plotted against time in Figure 4. It steadily increased with time and reached its maximum at 10–100 s (depending on $[C]_0$) then decreased gradually. Monomer consumption monitored at 295 nm ($\epsilon = 2.46 \times 10^3$ M^{-1} cm^{-1}) indicated that the polymerization rate was largest when ΔOD_{380} was maximal. The time–conversion curves were S shaped, corresponding to the steady increase in ΔOD_{380}. These facts suggest that the 380-nm band should be assigned to the propagating species of p-methoxystyrene (see below).

The short-wavelength absorption is presumably due to a π complex between the monomer and iodine. This complex has been reported to show an absorption at 325 nm in 2,2,4-trimethylpentane.[7] No further attempt was made to identify this peak.

Polymerization by Protonic Acid and Metal Halides. For further identification of the 380-nm peak, the reaction by the other initiators was examined in 1,2-dichloroethane ($[M]_0$ = 5.0 mM). Figures 5–7 show the results obtained with a protonic acid (CH_3SO_3H) and metal halides ($BF_3O(C_2H_5)_2$ and $SnCl_4$). In all three systems an intermediate absorption was commonly observed at 380 nm; the spectra were very similar to each other. The absorption spectra from 320 to 450 nm consisted of a single peak (380 nm), and there was no short-wavelength absorption as observed for iodine. Therefore, spectrum resolution as for the iodine system was not necessary in these cases.

ΔOD_{380} steadily increased with time in a time scale of seconds and then decreased after its maximum (Figures 5a–7a).

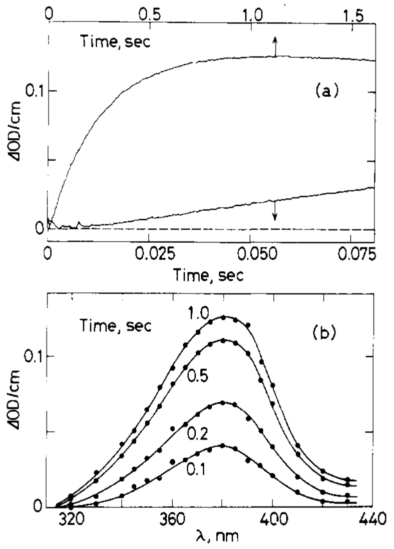

Figure 5. Intermediate formation in the *p*-methoxystyrene/CH_3SO_3H system in 1,2-dichloroethane at 30°C: (a) absorbance change at 380 nm; (b) time-resolved spectra. $[M]_0$ = 5.0 mM; $[C]_0$ = 5.0 mM.

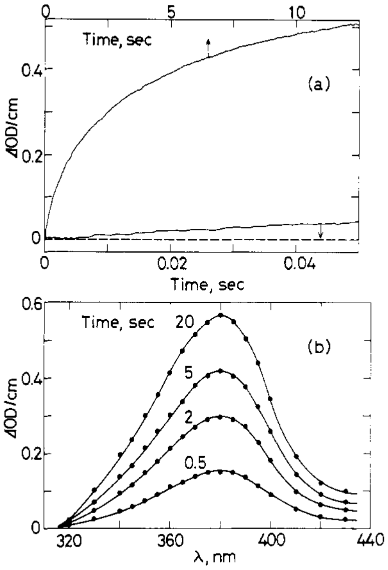

Figure 6. Intermediate formation in the *p*-methoxystyrene/$BF_3O(C_2H_5)_2$ system in 1,2-dichloroethane at 30 °C: (a) absorbance change at 380 nm; (b) time-resolved spectra. $[M]_0$ = 5.0 mM; $[C]_0$ = 0.50 mM.

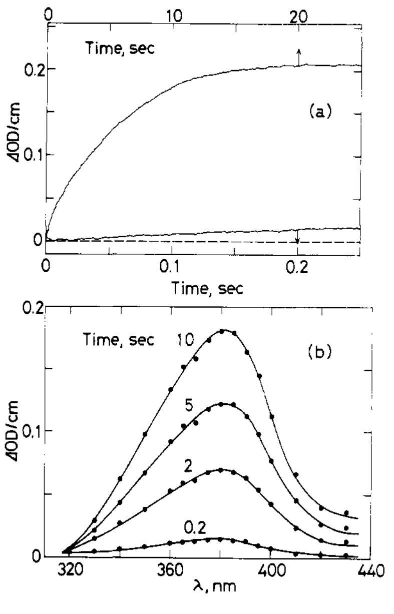

Figure 7. Intermediate formation in the *p*-methoxystyrene/$SnCl_4$ system in 1,2-dichloroethane at 30 °C: (a) absorbance change at 380 nm; (b) time-resolved spectra. $[M]_0$ = 5.0 mM; $[C]_0$ = 0.030 mM.

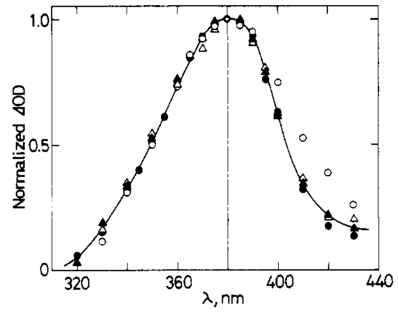

Figure 8. Normalized absorption spectrum of the intermediate obtained with four different initiators in 1,2-dichloroethane at 30 °C: (○) iodine; (●) CH_3SO_3H; (▲) $BF_3O(C_2H_5)_2$; (△) $SnCl_4$.

The formation rate of the intermediate depended on the initiators. Relative initiation rates ($(d\Delta OD_{380}/dt)_{t=0}/[C]_0[M]_0$) were in the order iodine < $CH_3SO_3H \ll BF_3O(C_2H_5)_2 \lesssim SnCl_4$, indicating that the metal halides can form the intermediate much faster than the other two initiators. Therefore, the metal halides required very small $[C]_0$ (0.030–0.50 mM) compared with $[C]_0$ = 5.0 mM for CH_3SO_3H and iodine to generate an appreciable absorption at 380 nm. Interestingly, while the above order of initiation rate followed the empirical activity of initiators, propagation rate constants, as shown later, depended little on the kind of initiators.

Identification of the Spectra and Kinetics. A common absorption band was observed at 380 nm in the reactions of *p*-methoxystyrene with the four initiators. It should be emphasized that a wide variety of cationic initiators (iodine, protonic acid, and metal halides) gave almost identical absorption spectra. This is clearly demonstrated by the single normalized spectrum shown in Figure 8, where spectra normalized at 380 nm were plotted for the four initiators. Therefore, the absorption centered at 380 nm must be assigned to a common intermediate derived from the monomer. The gradual decrease in ΔOD_{380} after its maximum rules out the possibility that this absorption comes from a stable reaction by-product. The qualitative correlation between ΔOD_{380} and rate of monomer consumption, described above for the iodine system, suggests that the observed species is a true polymerization intermediate, i.e., the propagating species.

The λ_{max} value of 380 nm also seems to be reasonable for the propagating species derived from *p*-methoxystyrene. For example, one of us[8] previously reported that a mixture of *p*-methoxystyrene and $BF_3O(C_2H_5)_2$ in 1,2-dichloroethane exhibits a strong absorption at about 365 nm at room temperature. The polystyryl[9] and benzyl[10] cations have been reported to show peaks at 340 and 363 nm, respectively, in 1,2-dichloroethane. The observed bathochromic shift for poly(*p*-methoxystyryl) cation most likely resulted from the stabilization of cationic center by the electron-donating *p*-methoxy group. A recent ^{13}C-NMR analysis[11] shows that introducing a *p*-methoxy group to the α-styryl cation increases the electron density at the cationic center.

The above identification of the 380-nm band is quantitatively supported by the kinetic treatment described below. If the propagating species has an absorption at 380 nm, the monomer consumption rate is expressed as:

Table I
Kinetic and Spectroscopic Data for *p*-Methoxystyrene Polymerization in 1,2-Dichloroethane at 30 °C ($[M]_0 = 5.0 \times 10^{-3}$ M)

Initiator	$[C]_0 \times 10^3$, M	k_p/ϵ_{380}, cm/s	$k_p \times 10^{-3}$,[a] $M^{-1} s^{-1}$	$[P^*]_{max} \times 10^6$,[a] M	$([P^*]_{max}/[C]_0) \times 10^2$
I_2	2.5	0.13	3.6	2.2	0.088
		0.17	4.7	2.1	0.086
	5.0	0.17	4.7	5.8	0.12
		0.17	4.8	5.5	0.11
	7.5	0.17	4.7	7.9	0.11
		0.18	5.0	8.2	0.11
	15	0.18	4.9	22	0.15
CH_3SO_3H	3.0	0.73	21	1.9	0.064
	5.0	0.82	23	4.5	0.090
$BF_3O(C_2H_5)_2$	0.30	0.22	6.1	15	4.9
	0.50	0.21	6.0	21	4.2
	1.0	0.23	6.4	31	3.1
$SnCl_4$	0.030	0.44	12	7.4	25
	0.050	0.38	11	14	27
	0.15	0.40	11	41	28

[a] $\epsilon_{380} = 2.8 \times 10^4$ M^{-1} cm^{-1}.[8]

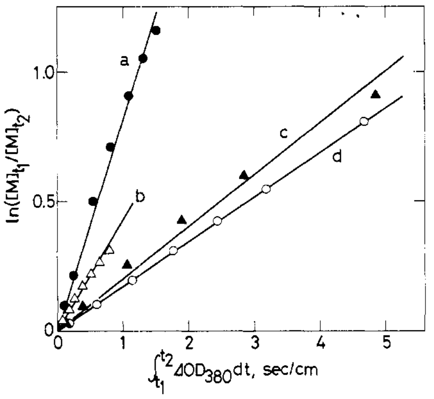

Figure 9. Plots of eq 2 for the *p*-methoxystyrene polymerizations in 1,2-dichloroethane at 30 °C: $[M]_0 = 5.0$ mM. Initiator: (a) CH_3SO_3H, 5.0 mM; (b) $SnCl_4$, 0.030 mM; (c) $BF_3O(C_2H_5)_2$, 0.50 mM; (d) iodine, 5.0 mM.

$$-\frac{d[M]_t}{dt} = k_p[P^*][M]_t = k_p \frac{\Delta OD_{380}}{\epsilon_{380}} [M]_t \qquad (1)$$

where k_p is the propagation rate constant and ϵ_{380} is the molar absorptivity of the 380-nm peak; $[P^*]$ and $[M]_t$ represent the concentrations of the propagating species and the monomer, respectively, at time t. Integration of eq 1 from $t = t_1$ to t_2 gives:

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = \frac{k_p}{\epsilon_{380}} \int_{t_1}^{t_2} \Delta OD_{380}\, dt \qquad (2)$$

In most cases t_1 may be taken as zero. The left-hand side of eq 2 can be determined from the monomer consumption monitored at 295 nm. Graphical integration of ΔOD_{380} vs. time plots (e.g., Figures 4 and 5a) affords the integral in eq 2. Thus, plots of eq 2 were obtained and their typical examples are shown in Figure 9. The plots for the four initiators were all straight lines through the origin, which clearly shows that the 380-nm peak is quantitively related to the propagating species. Data at other initiator concentrations than those in Figure 9 also gave similar straight lines.

Slopes of the straight lines gave k_p/ϵ_{380} values, from which propagation rate constants were determined with the assumption that $\epsilon_{380} = 2.8 \times 10^4$ M^{-1} cm^{-1}.[12] Table I lists these values obtained with a variety of initiators at various concentrations ($[C]_0$). The k_p values for respective initiators were independent of $[C]_0$ in the range of $[C]_0$ examined here, showing the reasonableness of our kinetic treatment. In Table I are also summarized the maximal concentrations of the propagating species ($[P^*]_{max}$). Results of duplicate experiments for the iodine system show a good reproducibility.

k_p Values. The k_p values for the four systems range from 4×10^3 to 2×10^4 M^{-1} s^{-1} and seem reasonable when compared with the reported value for $(C_6H_5)_3C^+SbCl_6^-$ initiator ($(1.2–1.6) \times 10^4$ M^{-1} s^{-1} in CH_2Cl_2 at 25 °C).[13] They are nearly independent of the initiators, indicating that the nature of the propagating species in 1,2-dichloroethane does not depend on counterions. The following two evidences suggest involvement of free ionic propagating species: (1) Addition of a common-ion salt ($(n\text{-}C_4H_9)_4NI$) to a *p*-methoxystyrene/iodine system in 1,2-dichloroethane clearly suppressed the 380-nm peak in absorption spectra and, correspondingly, monomer consumption rate was reduced. (2) The molecular weight of polymeric products, obtained under nearly the same conditions as in the spectroscopic measurements, was independent of the initiators ($(6.5–8) \times 10^3$ with iodine; ~6.5 × 10^3 with CH_3SO_3H; $[M]_0 = 10$ mM, $[C]_0 = 5.0$ mM, in 1,2-dichloroethane).

The second evidence also shows that the polymer molecular weights are much smaller than $[M]_0/[P^*]_{max}$ (see Table I) and hence that the present *p*-methoxystyrene systems are transfer dominant, as usually observed in most cationic polymerizations of vinyl monomers.

$[P^*]_{max}$ Values. In contrast to the independence of the k_p values, $[P^*]_{max}$ strongly depended on the nature of initiators. The last column ($[P^*]_{max}/[C]_0$) of Table I shows this dependence. With iodine and CH_3SO_3H, $[P^*]_{max}$ was much smaller than $[C]_0$ (about 0.1% of $[C]_0$), whereas with the metal halides, $[P^*]_{max}$ amounted to 5–25% of $[C]_0$. It is of interest that the former compounds are known as "weak" initiators and the latter as "strong" (active) initiators. The empirical activity order of initiators, therefore, may reflect principally not the reactivity (k_p) of the propagating species derived from them, but their initiation efficiencies indicated by $[P^*]_{max}/[C]_0$. In this context trifluoromethanesulfonic acid (CF_3SO_3H) appears to be interesting as initiator, because this acid is as active as metal halides[14] but its structure is very similar to that of CH_3SO_3H, a weak initiator. The *p*-methoxystyrene polymerization by CF_3SO_3H is now being studied by the stopped-flow method in our laboratory.

In conclusion, the present work has established a method to quantitatively determine the concentration of propagating species and hence its propagation rate constant (k_p) in cationic polymerization. Stopped-flow spectroscopy has successfully been applied to the determination.

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Acetylene Terminated Phenyl-*as*-triazine Oligomers and Polymers Therefrom[1a]

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ABSTRACT: Acetylene-terminated phenyl-*as*-triazine oligomers (ATPT) were prepared by two methods. Method 1 involved the preparation of amidrazone-terminated phenyl-*as*-triazine oligomers which were subsequently end capped with 4-(4-ethynylphenoxy)benzil to yield ATPT. Method 2 involved the direct preparation of ATPT from the reaction of the diamidrazone, the bisbenzil, and 4-(4-ethynylphenoxy)benzil. The ATPT prepared by method 2 exhibited better solubility, higher heats of reaction, lower polymer melt temperatures, and after thermal cure higher glass transition temperatures than those prepared by method 1. Preliminary adhesive and composite work was performed with one ATPT. Two acetylene-containing phenyl-*as*-triazine model compounds were prepared and characterized by high-pressure liquid chromatography and mass spectroscopy. The thermal reactions of the two model compounds were studied.

Linear polyphenyl-*as*-triazines are high-temperature thermoplastics with good long-term thermooxidative stability at 533 K (260 °C).[2a] However, at 533 K under load, these polymers undergo thermoplastic deformation. Previous attempts to thermally cross-link these polymers through nitrile and cyanato groups located on the pendant phenyl group attached to the *as*-triazine ring were only moderately successful.[2b] The polymers containing the cyanato groups were not processable due to the fast reaction of the cyanato groups. Whereas high temperatures were required to induce reaction of the nitrile groups which resulted in thermal degradation of the *as*-triazine ring.

Acetylene groups have recently been used to chain extend and cross-link oligomeric phenylenes,[3] imides,[4] phenylquinoxalines,[5] and ether ketone sulfones;[6] to rigidize and/or cross-link polyphenylquinoxalines[7] and polyimides;[8] and to serve as reactive plasticizers for polysulfones[9] and polyphenylquinoxalines.[10] Acetylene-terminated phenylquinoxaline oligomers were recently prepared by the reaction of 4-(4-ethynylphenoxy)benzil with *o*-diamino end-capped phenylquinoxaline oligomers and subsequently thermally polymerized.[11] Since the synthesis of polyphenylquinoxalines and polyphenyl-*as*-triazines employs a common monomer, the bis(1,2-dicarbonyl) compound, 4-(4-ethynylphenoxy)benzil, was used to prepare acetylene-terminated phenyl-*as*-triazine oligomers as described herein. This work was performed in an attempt to obtain polymers containing the phenyl-*as*-triazine ring with improved processability and structural integrity at temperatures as high as 533 K.

Experimental Section

Monomers and Reactants. The monomers and reactants for model compound work listed in Table I were prepared through known procedures or a slight modification thereof.

Perfluorobutyramidrazone. This compound was prepared by bubbling perfluorobutyronitrile slowly through a solution of 97% hydrazine in 2-propanol at 278 K (5 °C). After complete addition, the solution was stirred at ambient temperature for 2 h followed by removing the 2-propanol under vacuum at <303 K (30 °C). A white crystalline solid formed which was isolated, washed with cold 2-propanol, and recrystallized from cyclohexane to yield white platelets of perfluorobutyramidrazone, mp 342–342.5 K (69.0–69.5 °C).

2-Pyridylamidrazone. 2-Cyanopyridine was reacted with hydrazine in ethanol following a known procedure[13] to provide a pale yellow solid which was recrystallized from benzene to yield white needles, mp 367–368 K (94–95 °C).

Oxalamidrazone. According to a known procedure,[14] dicyanogen was bubbled through a cold solution of hydrazine in ethanol to provide pale yellow crystals, mp 451–452 K (178–179 °C) dec [introduced into preheated oil bath at 433 K (160 °C)].

Perfluoroadipamidrazone. The diamidrazone was prepared as previously reported[15] from the reaction of perfluoroadiponitrile with hydrazine in 2-propanol. White crystals, mp 456–457 K (183–184 °C) dec [introduced into pretreated oil bath at 443 K (170 °C)] were obtained after recrystallization from a mixture of 2-propanol and water.

2,6-Pyridinediyl Diamidrazone. 2,6-Dicyanopyridine was reacted with hydrazine in ethanol according to a known procedure[16] to provide a yellow solid. The crude 2,6-pyridinediyldiamidrazone was recrystallized by adding it to water preheated to 353 K (80 °C) to effect dissolution. Prolonged heating and higher temperatures resulted in partial degradation of the diamidrazone. Pale yellow needles, mp