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(27) ^{31}P nmr shifts (in ppm relative to 85% H_3PO_4 in water) were correlated with the presence of the following species: −19.4 $(NPCl_2)_3$; −11.4, terminal PCl_3 group; +7 $(NPCl_2)_4$ or $(-NPCl_2-)_4$ units; +15.3 to 17.24 $(-NPCl_2-)_{5 \text{ or } 6}$ units; +18 $(-NPCl_2-)_{7 \text{ or } 8}$ units; +300, PCl_6^- (probably as an end-capping unit).
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Effects of Mercaptides on Anionic Polymerization. IV. Polymerization of Styrene by Thiophenoxides in Polar Aprotic Solvents

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ABSTRACT: It was found, surprisingly, that sodium thiophenoxide initiates the polymerization of styrene in polar aprotic solvents such as *N,N'*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexamethylphosphoramide (HMPA). It initiated nearly no polymerization in less polar solvents such as benzene, toluene, dioxane, dimethoxyethane, and tetrahydrofuran. The active species that initiated the polymerization of styrene in the polar aprotic solvents was found to be sodium thiophenoxide itself by means of the identification of end groups of the oligomers. The activation energy for the polymerization of styrene by the mercaptide in DMF was 5.7 kcal/mol. Kinetic studies on the polymerization of styrene by the mercaptide in DMF were also made, and it was found that a living type polymerization occurred. The initiation reaction was found to be very slow and increased with increasing polymerization time. The rate constant of the propagation reaction (k_p) was 1.00×10^4 l. mol^{-1}/hr^{-1} (in DMF at 20°).

Styrene has been known to polymerize anionically when initiated by many organometallic compounds in solvents such as tetrahydrofuran, dimethoxyethane or dioxane to form living polymers.[1] The anionic polymerization of styrene (Alfrey–Price e value of styrene = −0.80), however, does not occur so readily compared with that of monomers having higher $+e$ values such as methacrylonitrile (e = +0.81),[2] acrylonitrile (e = +1.20),[2] and vinylidene cyanide (e = +2.58),[2] etc., that easily polymerize anionically even by the weak bases.[3] Thus, anionic polymerization of styrene necessitates the use of strongly basic initiators.

As described briefly in our previous papers,[3,4] sodium thiophenoxide, having a lower pK_a value than the general anionic initiators hitherto known, was also found surprisingly to initiate the polymerization of styrene in polar aprotic solvents such as *N,N'*-dimethylformamide (DMF), hexamethylphosphoramide (HMPA), or dimethyl sulfoxide (DMSO) under ordinary polymerization conditions. It did not, however, initiate polymerization in less polar solvents, such as benzene, toluene, dioxane, or tetrahydrofuran. These results suggest that new active species are formed by reactions between the mercaptide and polar aprotic solvents.

In this paper, the active species in the polar aprotic solvents that initiated the polymerization of styrene was confirmed by the same fashion as the previous papers.[4] The activation energy was also investigated for the polymerization of styrene in DMF between 0 and 30°. The kinetics of the polymerization of styrene by sodium thiophenoxide in DMF solvent were also studied.

Experimental Section

Reagents. Polar Aprotic Solvents. Commercially available products were refluxed over finely divided calcium hydride overnight and then distilled at reduced pressure just before use: hexamethylphosphoramide (HMPA), 66° (0.5 mm); dimethyl sulfoxide (DMSO), 86° (25 mm); *N,N'*-dimethylformamide (DMF), 76° (39 mm).

Styrene. Commercially available monomer was washed several times with 10% sodium hydroxide solution and then water. The monomer was dried with anhydrous calcium chloride and then distilled under nitrogen at reduced pressure. The middle fraction was freshly distilled immediately before use over calcium hydride at 48° (20 mm).

Sodium Thiophenoxide. This mercaptide was prepared in a three-necked flask, equipped with a stirrer, an argon gas inlet, and a condenser protected by a calcium chloride tube, by the addition of thiophenol to freshly cut sodium in dry ether, under an argon atmosphere. After refluxing and vigorous stirring for about 10 to 20 hr, the solvent was distilled off under a stream of argon.[5,6]

Polymerization. The polymerizations were carried out in sealed glass tubes. Precautions were taken to remove traces of moisture and air. To the glass tube was added styrene and aprotic solvent. This solution was cooled to −78° and the sodium thiophenoxide solution was added. Polymerization at 30° proceeded slowly and

Table I
Effect of Polar Aprotic Solvents on the Polymerization Rate of Styrene with Sodium Thiophenoxide at 30°[a]

Solvent	Polymer yield (%) conversion after 12 hr
HMPA	32
DMF	14
DMSO	9
THF, dioxane	0
Benzene, toluene	

[a] [St] = 3.48 mol/l., [Phenyl-SNa] = 3.00×10^{-2} mol/l.

the solution gradually developed a reddish color, due to the styrene anion. After a period of time, the reaction mixture was poured into a large excess of methanol containing dilute hydrochloric acid. The polymer that precipitated was collected and dried under reduced pressure at room temperature to constant weight.

Intrinsic Viscosity. The viscosities of the polymers obtained were measured in benzene by use of an Ubbelohde viscometer at 30°. The number average degree of polymerization was calculated from the relationship[7]

$$\log \overline{Pn} = 3.248 + 1.40 \log [\eta] \quad (1)$$

The molecular weights of polymer of low degree of polymerization were measured using a Knauer vapor pressure osmometer in benzene.

Sulfur Analysis. The sulfur contents of the oligomers were qualitatively confirmed by the sodium fusion method and quantitatively by the method of Schoniger.[8]

Measurement of Infrared Spectra. The infrared spectra of the oligomers obtained by sodium thiophenoxide in polar aprotic solvents were measured with a Hitachi Perkin-Elmer Model 337 double-beam spectrometer over the region of 4000 to 600 cm^{-1}.

Results and Discussion

Sodium thiophenoxide did not initiate the polymerization of styrene (St) in ordinary nonpolar solvents. On the other hand, it initiated the polymerization of styrene quite well in polar aprotic solvents, as is shown in Table I.

These results suggest that new active species are formed between the mercaptide and polar aprotic solvents. The copolymerization of styrene with methyl metacrylate (MMA) (mol ratio 1:1) was carried out with the use of sodium thiophenoxide in HMPA at 30°, and the molar fraction of MMA in the obtained copolymer was 0.95. The polymerization reaction was thus considered to be an anionic polymerization. To recognize the active species in the initiation reaction, methanol-soluble oligomers were prepared at a molecular ratio of the monomer (4.37 mol/l.) to sodium thiophenoxide (13.2 mol/l.) of 1 to 3 in the polar aprotic solvents at room temperature under a stream of nitrogen with vigorous stirring. The oligomers obtained were purified. Qualitative and quantitative analyses for sulfur in the polymer and measurements of infrared spectra and molecular weight determination were then carried out.

The sulfur contents in the oligomers were clearly confirmed in all cases by the sodium fusion method, and by infrared absorption at 690 cm^{-1} due to the C–S bond (Figure 1). An oligomer having a molecular weight of 670 had a sulfur content of 4.8%. This result indicates that each polymer chain contains one sulfur atom. Thus, it may be concluded that the active species in the polymerization is sodium thiophenoxide.

In general, pK_a values are affected by the following external conditions:[9] (1) solvent, (2) temperature, (3) pressure, and (4) light. In the polymerization systems described here, only solvent affects must be taken into account. The pK_a value of thiophenol decreases only slightly with increasing dielectric constants (D_K) of the solvent. To cite a few instances,[10] pK_a = 8.6 (in $(CH_3)_2CO$–H_2O, D_K = 35), pK_a = 8.6 (in C_2H_5OH–H_2O, D_K = 35), pK_a = 8.3 (in C_2H_5OH–H_2O), pK_a = 7.5 (in *tert*-C_4H_9OH–H_2O, D_K = 70), and pK_a = 6.5 (in H_2O, D_K = 80). This fact is also clear from calculations based on the method of Elliott and Kilpatrick.[11] The pK_a value of thiophenoxide decreases only slightly in polar aprotic solvents, compared with less polar solvents, such as benzene, toluene, dioxane, and te-

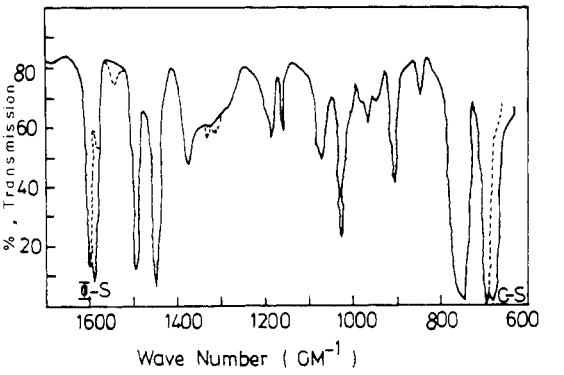

Figure 1. Infrared spectrum of oily oligomer obtained by sodium thiophenoxide in HMPA solvent: (—) oily oligomer; (---) pure polystyrene film.

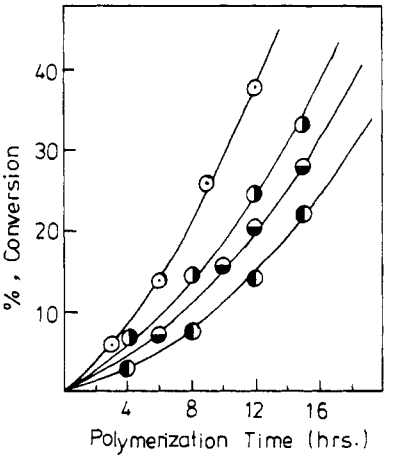

Figure 2. Polymerization of styrene by various concentrations of sodium thiophenoxide in DMF solvent at 30°; [styrene] = 3.48 mol/l.; [phenyl-SNa] = (○) 7.5×10^{-2}, (◑) 6.0×10^{-2}, (◒) 4.5×10^{-2}, (◐) 3.0×10^{-2} mol/l.

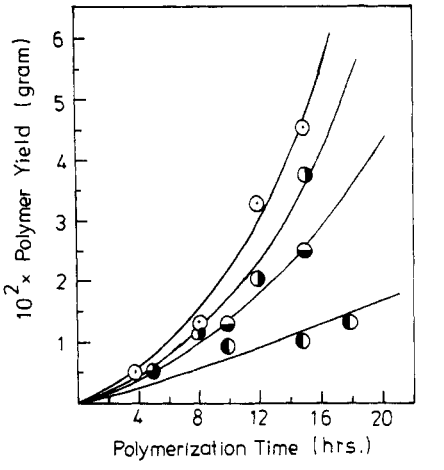

Figure 3. Polymerization of styrene by various concentrations of monomer in DMF solvent in 30°; [phenyl-SNa] = 6.00×10^{-2} mol/l.; [styrene] = (○) 4.35, (◑) 3.48, (◒) 2.61, (◐) 1.74 mol/l.

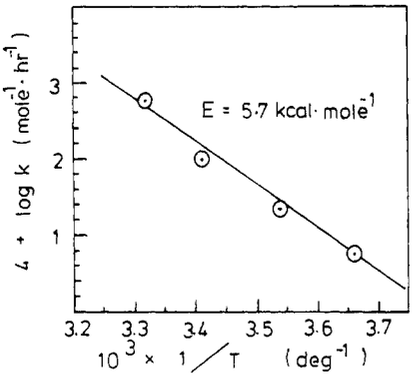

Figure 4. Arrhenius plot for polymerization of styrene by sodium thiophenoxide in DMF solvent; [styrene] = 3.48 mol/l, [phenyl-SNa] = 6.00×10^{-2} mol/l.

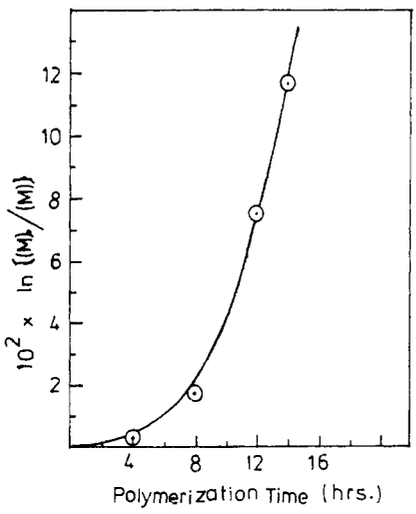

Figure 5. Relationship between ln $[[M]_0/[M]]$ and polymerization time in DMF solvent at 30°; [styrene] = 4.35 mol/l., [phenyl-SNa] = 6.00×10^{-2} mol/l.

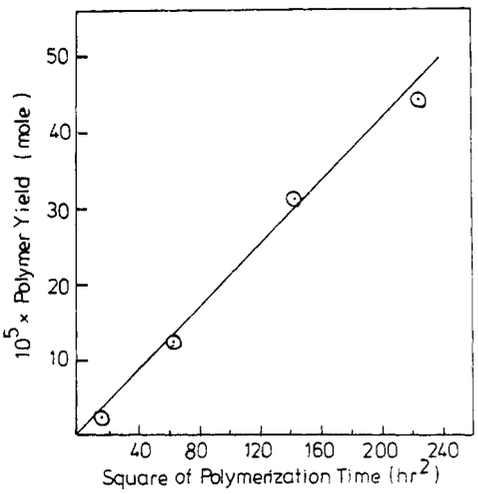

Figure 6. Relationship between polymer yield and square of polymerization time in DMF solvent at 30°; [styrene] = 4.35 mol/l., [phenyl-SNa] = 6.00×10^{-2} mol/l.

trahydrofuran.[10] The polarizability of the mercaptide, however, increases very much in polar aprotic solvents, as compared with other ordinary solvents. The nucleophilic reaction is, as already described in the previous papers,[3,4] determined by: (a) basicity, (b) polarizability, and (c) the α effect of the nucleophide. Polarizability, rather than pK_a

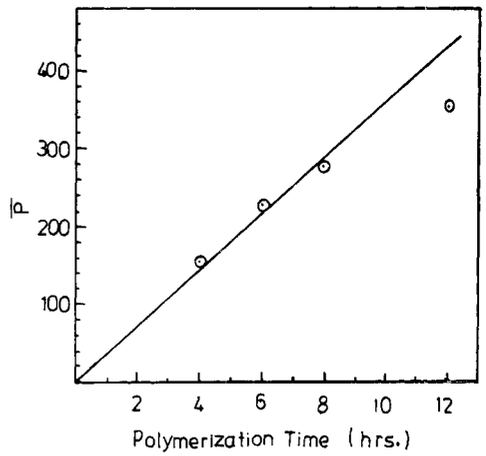

Figure 7. Relationship between number average degree of polymerization (P) and polymerization time in DMF solvent at 20°; [styrene] = 3.48 mol/l., [phenyl-SNa] = 6.00×10^{-2} mol/l.

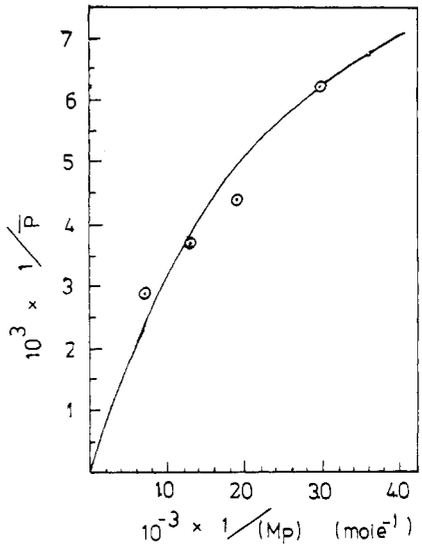

Figure 8. Relationship between $1/P$ and $1/[M_p]$; [styrene] = 3.48 mol/l., [phenyl-SNa] = 6.00×10^{-2} mol/l. in DMF solvent at 20°.

value, plays an important role for the initiation reaction of anionic polymerization. Thus, the unusually enhanced reactivity of the mercaptide in polar aprotic solvents compared with less polar solvents can also be attributed to the enhanced polarizability of the mercaptide despite the slight decrease in the pK_a value.

As is shown in Table I, the relative effects of polar aprotic solvents in the reactivity of sodium thiophenoxide decreased in the order of HMPA (D_K = 30) > DMF (D_K = 37) > DMSO (D_K = 45).[12] The effects were clearly independent on the dielectric constants of the solvents, and were dependent on solvating power.[12]

The basicity order of thiophenoxide in the solvents is also consistent with the effect of solvating power. However, the effect of basicity on reactivity is not an important factor in the polymerization reaction by thiophenoxide as already stated above. HMPA does not nearly solvate the anions.[12] On the other hand, DMSO highly solvates anions *via* its semipolar S–O bond. This solvent is believed to form relatively stable complexes with the catalyst, or with the active end of the growing chain.[13,14] The effects of polar aprotic solvents of the reactivity of sodium thiophenoxide obtained are thus quite reasonable.

The influence of mercaptide and monomer concentration

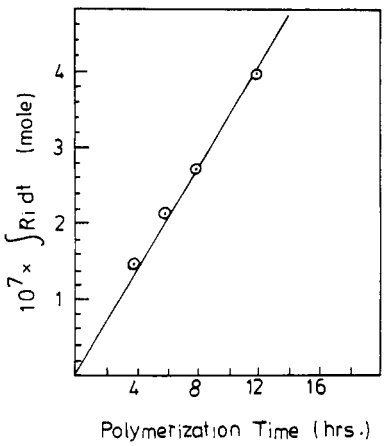

Figure 9. Relationship between polymerization time and $R_i dt$; [styrene] = 3.48 mol/l., [phenyl-SNa] = 6.00×10^{-2} mol/l. in DMF solvent at 20°.

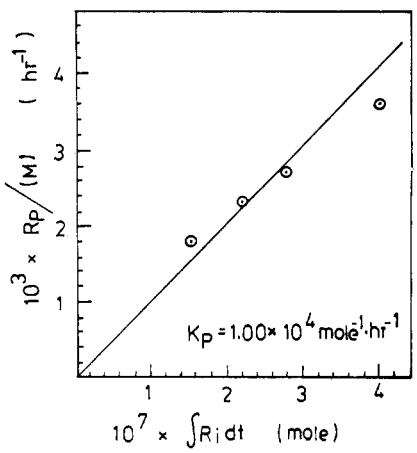

Figure 10. Relationship between $R_p/[M]$ and $R_i dt$; [styrene] = 3.48 mol/l., [phenyl-SNa] = 6.00×10^{-2} mol/l. in DMF solvent at 20°.

on the polymerization of styrene are shown in Figures 2 and 3. A remarkable acceleration effect on the rate of polymerization is observed with increasing polymerization time, especially when higher concentrations of the monomer or higher temperatures are used. From Figures 2 and 3, the initial rate of polymerization was found to depend on the first power of the concentrations of monomer and mercaptide.

The activation energy was obtained as $E = 5.7$ kcal/mol in the temperature region of 0 to 30° for the polymerization of styrene by sodium thiophenoxide in DMF solvent, whose Arrhenius plot is shown in Figure 4.

The relationship between ln $[[M]_0/[M]]$ and polymerization time is shown in Figure 5, and the relationship between polymer yield and the square of polymerization time is shown in Figure 6.

The number average degree of polymerization increased with increasing the polymerization time, as may be seen in Figure 7. Figures 5 to 7 indicate that termination is a negligible reaction.

The elementary reactions were thus assumed as follows initiation

$$C + M \xrightarrow{k_i} CM^* \quad R_i = k_i[C][M] \tag{2}$$

propagation

$$CM^* + M \xrightarrow{k_p} CM_2^*$$

$$P_{n-1}^* + M \xrightarrow{k_p} P_n^* \quad R_p = k_p[P_{n-1}^*][M] \tag{3}$$

where C, M, and P* represent the initiator, monomer, and active propagation species, respectively. R_i and R_p denote the rates of initiation and propagation, and k_i and k_p are the rate constants of the corresponding elementary reactions.

According to the graphical evaluation method of the rate constants by Kagiya and coworkers,[15] the following relationships apply to the elementary reactions assumed above

$$1/\bar{P} = \int R_i dt/[M_p] \tag{4}$$

$$R_p/[M] = k_p \int R_i dt \tag{5}$$

where $[M_p]$ and $\bar{P}$ are the polymer yield, counted in polymerized monomer moles, and the number average degree of polymerization, respectively. The relationship between $1/\bar{P}$ and $1/[M_p]$ is shown in Figure 8, from which the values of $\int R_i dt$ were obtained. The values of $\int R_i dt$ obtained were very small and increased with increasing polymerization time, as may be seen in Figure 9, in which the dependence of $\int R_i dt$ on the polymerization time is shown. The relationship between $R_p/[M]$ and $\int R_i dt$ is shown in Figure 10, in which reasonable value of $k_p = 1.00 \times 1^4$ l. mol^{-1}/hr^{-1} is obined.[16,20]

According to the classification of the polymerization from the kinetic point of view,[21] the polymerization system applied here is reasonably classified as the slow-initiated nonstationary successive type, that is a living type polymerization.

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