# Block copolymers by combination of cationic and radical routes: 5. Polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoyl chloride)*

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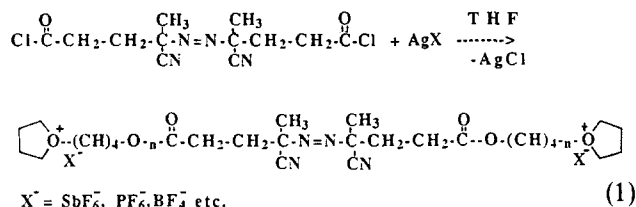*Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 80626, Turkey*

The kinetics of the polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) was investigated in bulk and in benzene solution at 60°C. It was found that the overall rate of polymerization is proportional to the 0.48 power of the initiator concentration. The chain transfer-to-initiator and chain transfer-to-solvent constants were estimated to be $C_I = 0.41$ and $C_S = 1.9 \times 10^{-4}$, respectively. Polymerization of styrene initiated by ACPC yields polystyrene with an acyl chloride terminal group at each end. Polymerization of tetrahydrofuran initiated by acyl chloride-terminated polystyrene in conjunction with $AgSbF_6$ provided the formation of a block copolymer.

## INTRODUCTION

We have previously established[1-3] that the synthesis of block copolymers by the combination of cationic and radical routes may be accomplished by a two-step procedure. First, 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) when reacted with a silver salt having low nucleophilic ions in the presence of tetrahydrofuran (THF) produces a diacyl cation and polymerization at both ends by an addition mechanism:

Cl-C-CH₂-CH₂-C-N=N-C-CH₂-CH₂-C-Cl + AgX ——→ (THF, -AgCl)

(structure with CH₃, CN groups)

$X^- = SbF_6^-,\ PF_6^-, BF_4^-$, etc. (1)

Detailed kinetic and mechanistic investigations[4] revealed that the resultant polytetrahydrofuran (PTHF) contains one (-N=N-) group in the main chain. Thermal decomposition of the azo linkage produces two polymeric radicals per chain, which gives rise to the formation of block copolymers in the presence of a monomer susceptible to free-radical polymerization (e.g. styrene):

PTHF~N=N~PTHF + CH₂=CH ——→ PTHF~[CH₂-CH]ₙ- CH₂-CH (2)
(Ph)
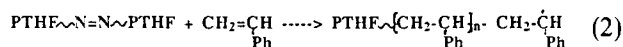
This type of block copolymer greatly depends on the kinetic behaviour of the monomer employed in the second step of the procedure.

A different sequence of the same procedure may also be used[3]. Polymerization of tetrahydrofuran initiated by polymers endowed with acyl chloride groups in conjunction with a silver salt provided the formation of block copolymers. One way[5] to produce polystyrene with acyl chloride end-groups is to react the living polystyrene with excess phosgene at 70°C. Dimerization of initial polystyrene molecules during phosgenation and termination by impurities contained in the phosgene were a deterrent to the use of this method. Alternatively, free-radical polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and subsequent treatment of these polymers with $PCl_5$ yielded two acyl chloride end-groups. This method suffers from the difficulty in treating a small amount of functional groups present in the long chain with $PCl_5$ and successive leaching for the removal of phosphorus oxychloride from the polymer. Therefore, it seemed suitable to use ACPC as a free-radical initiator for the polymerization of vinyl monomers, in order to obtain, directly, acyl chloride-terminated polymers having appropriate functionality for the subsequent cationic step leading to the formation of block copolymers. A similar approach[6] was applied to prepare block copolymers by reacting acyl chloride-terminated polystyrene with diols. The present work reports the kinetic studies of polymerization of styrene initiated by ACPC together with block copolymerization by means of the polystyrene obtained.

## EXPERIMENTAL

### Materials

Styrene and THF were used as free-radical and cationically polymerizable monomers, respectively, and were freed from inhibitors by conventional drying and distillation procedures. Benzene, n-hexane, methylene chloride and petroleum ether (40–60) were dried and distilled before use. $AgSbF_6$ (Aldrich), ACPA (Fluka) and $PCl_5$ (Merck) were used as-received. The corresponding diacid chloride ACPC was prepared according to a procedure described elsewhere[7].

## Free-radical polymerization

Bulk monomer styrene or the appropriate solution in benzene containing a known amount of ACPC were outgassed in the usual manner and placed in a thermostat at 60°C. At the end of polymerization, the reaction mixtures were poured into a 10-fold excess of methanol and the precipitated polymers filtered and dried. A gravimetric technique was used to determine the rates as well as the degree of polymerization. In all rate measurements the monomer conversion was less than 10% and the concentration of initiator [I] is assumed to be essentially constant. Molecular weights were determined from the solution viscosities at 30°C in toluene with the aid of the following equation[8]:

$$[\eta] = 1.1 \times 10^{-4} M^{0.725} \tag{3}$$

## Block copolymerization

Acyl chloride-terminated polystyrenes, which were used in the block copolymerization experiment, were obtained as described above, except that precipitation was in dry petroleum ether under a dry nitrogen atmosphere. The precipitated polymers were characterized by the infra-red band at 1800 cm$^{-1}$ (–COCl group). Appropriate solutions of acyl chloride-terminated polystyrenes and AgSbF$_6$ in THF were degassed in the usual manner. Polymerization and recovery of polymers were achieved as described previously[3]. G.p.c. chromatograms were obtained using a Knauer M 64 instrument using THF as the eluent and a flow rate of 1 ml min$^{-1}$. Molecular weights were calculated with reference to polystyrene standards.

## RESULTS AND DISCUSSION

### Kinetic study

ACPC was utilized as a free-radical initiator for the polymerization of styrene in bulk. ACPC has a particular advantage when bulk polymerization is desired, as it is soluble in common monomers as well as in common solvents, as opposed to the corresponding diacid. The results for bulk polymerization are given in *Table 1*. The simplest reaction scheme for vinyl polymerization in bulk when termination occurs by combination of polymer radicals in styrene polymerization leads to the following equation[9]:

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_I \frac{[I]}{[M]} + C_M \tag{4}$$

in which $C_I$ and $C_M$ are transfer constants to initiator and monomer, respectively; $\bar{P}_n$ is the number-average degree of polymerization; $R_p$ is the rate of polymerization; and $k_t$ and $k_p$ are termination and polymerization rate constants, respectively. The plot of the reciprocal

**Table 1** Bulk polymerization of styrene initiated by ACPC at 60°C$^a$

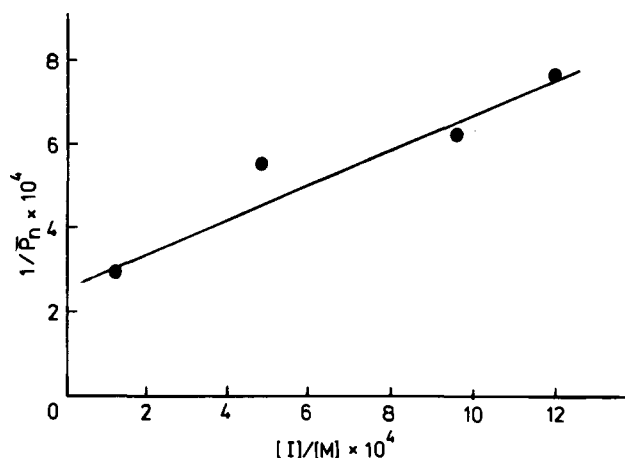| Run No. | [I] × 10³ (mol l⁻¹) | Yield (wt%) | $R_p$ × 10⁵ (mol l⁻¹ s⁻¹) | [η] (dl g⁻¹) | (1/$\bar{P}_n$) × 10⁴ |
|---------|---------------------|-------------|----------------------------|--------------|------------------------|
| 1 | 1 | 0.928 | 2.21 | 1.15 | 2.97 |
| 2 | 4 | 1.55 | 3.719 | 0.73 | 5.58 |
| 3 | 4 | 2.25 | 5.11 | 0.68 | 6.15 |
| 4 | 10 | 2.3 | 5.55 | 0.57 | 7.82 |
| 5 | 12 | 2.7 | 6.5 | 0.29 | 20.19 |

$^a$ [M] = 8.36 mol l⁻¹; polymerization time = 60 min



**Figure 1** Plot of the reciprocal number-average degree of polymerization 1/$\bar{P}_n$ versus [I]/[M] for the bulk polymerization of styrene at 60°C initiated by ACPC
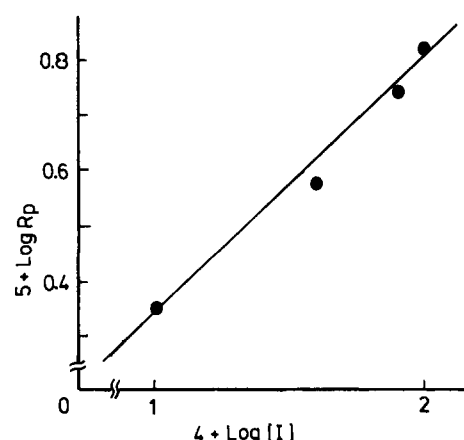


**Figure 2** Rate of polymerization as a function of initiator concentration at [M] = 8.36 mol l⁻¹ for the bulk polymerization of styrene at 60°C initiated by ACPC

number-average degree of polymerization (1/$\bar{P}_n$) against [I]/[M] is shown in *Figure 1*. The $C_I$ value for ACPC in styrene was calculated from the slope of the straight line to be $C_I = 0.41$. In general, azonitriles are hardly susceptible to transfer reaction and are commonly preferred as initiators in polymerization. However, our value is acceptable since the $C_I$ value increases with increasing electronegativity of substituent[10]. A plot of log $R_p$ against log[I] at constant [M] for ACPC is shown in *Figure 2*, where [I] again refers to the mean concentration of initiator in the system. There is a gradient of 0.48, which shows the general behaviour of this type of initiation. We have also studied the kinetics of polymerization of styrene initiated by ACPC in benzene, and the results are shown in *Table 2*. In order to determine $C_S$, the chain transfer-to-solvent constant, equation (4) was arranged for solution polymerization:

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p^2} \frac{R_p}{[M]} + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + C_M \tag{5}$$

and in another form:

$$\left(\frac{1}{\bar{P}_n} - C_M\right)[M] = C_I[I] + \frac{k_t}{k_p^2} \frac{R_p}{[M]} + C_S[S] \tag{6}$$

(1/$\bar{P}_n$ – $C_M$)[M] was plotted against [S]. This plot is represented in *Figure 3*. From the slope, $C_S$ was determined as $1.90 \times 10^{-4}$.
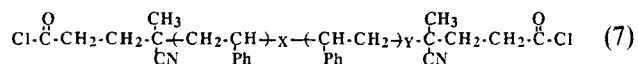
**Table 2** Bulk polymerization of styrene initiated by ACPC in benzene at 60°C[a]

| Run No. | $[I] \times 10^3$ (mol l$^{-1}$) | Yield (wt%) | $R_p \times 10^5$ (mol l$^{-1}$ s$^{-1}$) | $[\eta]$ (dl g$^{-1}$) | $(1/\bar{P}_n)$ $\times 10^4$ |
|---------|-----------|-------|-----------|-------|-------|
| 6 | 7.02 | 1.31 | 10.1 | 0.65 | 6.5 |
| 7 | 6.02 | 3.91 | 9.09 | 0.55 | 8.2 |
| 8 | 5.02 | 2.99 | 6.96 | 0.18 | 9.93 |
| 9 | 3.01 | 2.22 | 5.11 | 0.28 | 20.68 |
| 10 | 2.01 | 1.18 | 3.11 | 0.16 | 13.2 |

[a] $[I] = 8 \times 10^{-3}$ mol l$^{-1}$; polymerization time = 60 min
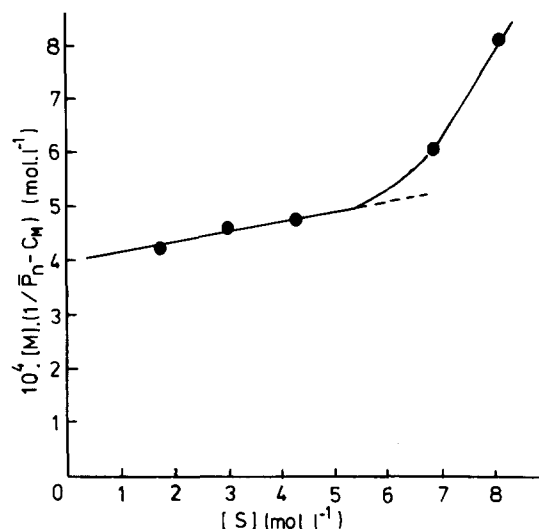


**Figure 3** $(1/\bar{P}_n - C_M)[M]$ as a function of $[S]$ for the polymerization of styrene in benzene at 60°C initiated by ACPC. $[I] = 8 \times 10^{-3}$ mol l$^{-1}$

*Block copolymerization*

Styrene polymerization by means of ACPC is expected to yield polystyrene molecules with an acyl chloride group at each end, since the termination reaction in styrene polymerization occurs by combination:

$$\underset{\text{CN}}{\overset{\text{O}}{\text{Cl-C-CH}_2\text{-CH}_2\text{-C}}}\underset{\text{Ph}}{\overset{\text{CH}_3}{\text{-C-(CH}_2\text{-CH)}_x}}\underset{\text{Ph}}{\overset{\text{CH}_3}{\text{-(CH-CH}_2)_y\text{-C}}}\underset{\text{CN}}{\overset{\text{CH}_3}{\text{-C}}}\underset{\text{}}{\overset{\text{O}}{\text{-CH}_2\text{-CH}_2\text{-C-Cl}}} \quad (7)$$

Whether or not the product polymer possesses one or two acyl chloride end-groups depends mainly on the ratio of disproportionation to combination for a particular polymerization. In either case oxocarbenium polymerization of THF may be accomplished essentially as indicated below:

$$\text{ClCO}\sim\text{pSt}\sim\text{COCl} + \text{THF} \xrightarrow{\text{AgSbF}_6} \text{Block copolymer} \quad (8)$$
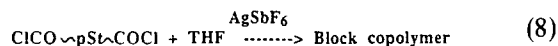
As a typical example, 0.4 g of acyl chloride-endowed polystyrene, which was obtained as described in the 'Experimental' section, in 20 ml of THF and 0.061 g of AgSbF$_6$ were mixed under nitrogen at 0°C. The precipitation of AgCl was quickly completed. After 3 h, the solution was precipitated into cold water containing a small amount of base. *Figure 4* shows the g.p.c. chromatograms of acyl chloride-terminated polystyrene and block copolymer produced from the oxocarbenium initiation. These chromatograms indicate the unimodal molecular-weight distribution in both cases and an increase in the molecular weight as a result of block copolymerization. The existence of block copolymer

formation was obtained by subjecting a portion of the product to ethanol extraction over 20 h. Homopolytetrahydrofuran, but not polystyrene, is soluble in ethanol, and this treatment did not remove any polymer from the sample. The infra-red spectra of the ethanol-treated block copolymer absorption peaks at 1725 cm$^{-1}$, similar to polytetrahydrofuran obtained by azooxocarbenium initiation[1], in addition to the usual absorption peaks of polystyrene (*Figure 5*). Furthermore, dual g.p.c. detection by refractive index and ultra-violet recording allowed a clear assignment of the block copolymer formation, as homopolytetrahydrofuran is transparent at the wavelength (254 nm) of the u.v. detector.

CONCLUSIONS

In conclusion, block copolymerization via cationic and radical routes provides a versatile two-stage method applicable to most nucleophilic and vinyl monomers. In principle, it should not matter which route is employed
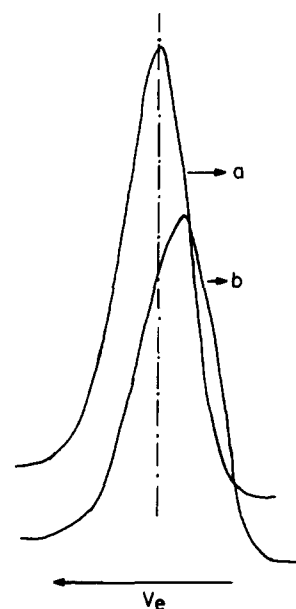


**Figure 4** G.p.c. chromatograms of: (a) polystyrene obtained by using ACPC, $\bar{M}_w = 125\,000$; (b) block copolymer of styrene and tetrahydrofuran, $\bar{M}_w = 180\,000$. RI detector
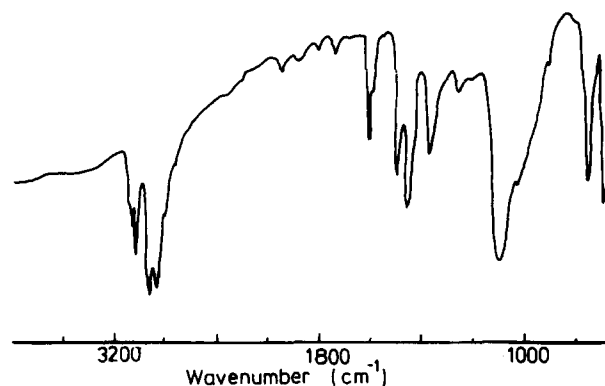


**Figure 5** Infra-red spectrum of polystyrene/polytetrahydrofuran block copolymer

first. The overall structure of block copolymer is determined by the structure of the prepolymer, which itself requires knowledge of the reactivity of the initiator and of the reaction kinetics. It is clear that this procedure can be used to prepare AB- and ABA-type block copolymers according to the kinetic behaviour of free-radical polymerizable monomer involved.

## ACKNOWLEDGEMENTS

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