Block copolymers by combination of cationic and radical routes: 4. Cationic polymerization of tetrahydrofuran initiated by difunctional azo-oxocarbenium initiator*

Gürkan Hızal and Yusuf Yağcı†
Technical University of Istanbul, Department of Chemistry, Maslak, Istanbul 80626, Turkey
(Received 10 June 1988; accepted 7 October 1988)

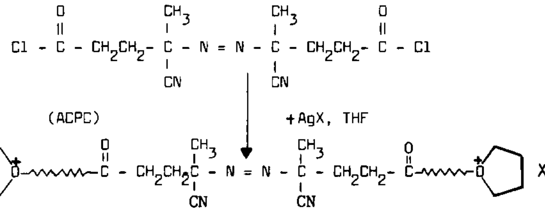
The kinetics of the bulk polymerization of tetrahydrofuran initiated by 4,4-azobis(4-cyanopentanoyl chloride) in conjunction with silver salts have been studied at −20, 0 and 10°C. Propagation rate constants increase with increasing temperature ($k_p = 4.7 \times 10^{-4}$ at −20°C, 3.7×10^{-3} at 0°C and $1.2 \times 10^{-2}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ at 10°C) and an Arrhenius plot gives an activation energy of $57.6\,\mathrm{kJ\,mol^{-1}}$. The enthalpy and entropy changes were estimated to be $\Delta H_p = -24\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S_p^\circ = -86.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ respectively. Spectroscopic and degradation studies showed that polymers obtained via this initiation method contained one azo linkage per macromolecule chain.

(Keywords: block copolymer; cationic polymerization; azo-oxocarbenium initiator; azo linkage)

INTRODUCTION

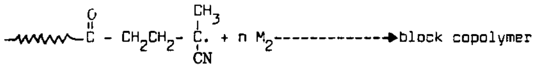
There has been an enormous amount of interest in block copolymers, owing to their use as thermoplastics, elastomers, adhesives, etc. The synthesis, characterization and properties of block copolymers have recently been reviewed by several authors[1–3]. Transformation reactions extend the range of possible monomer combinations in block copolymers[3].

Recently, Yağcı presented[4–6] a new conceptual approach to preparing block copolymers by cation-to-radical and reverse transformation polymerization. The method involves a two-stage procedure. First, synthesis of a polytetrahydrofuran (PTHF) containing one azo linkage in the main chain by the use of a difunctional azo-oxocarbenium initiator:



(1)

and then decomposition of the azo linkage, which gives rise to the formation of block copolymers in the presence of a monomer susceptible to radical polymerization:



$$\sim\!\sim\!\sim\overset{O}{\overset{\|}{C}}-CH_2CH_2-\underset{CN}{\overset{CH_3}{C\cdot}}+n\,M_2 \dashrightarrow \text{block copolymer} \qquad (2)$$

A different sequence of this procedure may also be employed[6].

A common feature of both methods is that the overall structure of the block copolymers depends on the mode of termination of the free-radical polymerization step. Moreover, the polymerization conditions of both cationic and free-radical steps are expected to govern the chain lengths of PTHF and polyvinyl sequences of block copolymers, respectively. Therefore, we have investigated kinetic and mechanistic details of the cationic polymerization of tetrahydrofuran (THF) initiated by a so-called azo-oxocarbenium initiator together with the thermal decomposition of the azo-linked PTHF obtained. Detailed investigations of the free-radical polymerization step by means of azo-linked PTHF will be the subject of future publications.

EXPERIMENTAL

Materials

THF was purified by conventional drying and distillation procedures. $AgSbF_6$, $AgBF_4$ and 4,4-azobis(cyanopentanoic acid) (Fluka) were used without further purification. The corresponding diacid chloride (ACPC) solution was prepared according to a previously described procedure[7].

Polymerization procedures

Polymerizations were carried out under a dry nitrogen atmosphere. Appropriate stock solutions of silver salts ($AgSbF_6$ or $AgBF_4$) and ACPC in THF were prepared by distillation of THF in a high-vacuum system. The polymerizations were initiated by mixing the two solutions, by means of a syringe, in a reaction vessel sealed under

---

* Dedicated to Professor A. C. Aydoğan on the occasion of his retirement

† To whom correspondence should be addressed

0032-3861/89/040722-04$03.00

nitrogen. Upon mixing at the defined reaction temperature, the precipitation of AgCl was quickly completed. After a given time of reaction, the polymerization was terminated by addition of methanol.

The polymer was filtered in order to remove AgCl, and precipitated in cold water. The polymer was then dried in vacuum, weighed and characterized.

Characterization of PTHF

The molecular weights of PTHF were estimated from solution viscosities in benzene at 30°C with the aid of the relationship[8]:

$$[\eta]=1.31\times10^{-3}\bar{M}_n^{0.6} \qquad (3)$$

G.p.c. chromatograms were obtained using a Knauer M64 instrument with methyl ethyl ketone as the eluent and a flow rate of 1 ml min^{-1}. Molecular weights were calculated by reference to polystyrene standards. The u.v. and ^{1}H n.m.r. spectra of sodium-phenoxide-terminated polymers were recorded, respectively, on a Shimadzu-U.V. 150-02 and a Bruker AC-200 spectrometer operating at 200 MHz.

Degradation of polymers

The thermal degradation of PTHF was carried out in benzene solution containing excess diphenylpicrylhydrazyl (DPPH) as a radical scavenger. Degassed solutions were heated at 60°C. At the end of a given time, viscosities were measured.

RESULTS AND DISCUSSION

Bulk polymerizations of THF initiated using combinations of ACPC and $AgSbF_6$ were carried out at -20, 0 and 10°C. In *Figure 1* data are plotted for monomer conversions *versus* time for the three temperatures. It is seen that equilibrium conversions of 95.5, 88.0 and 84.0% for the corresponding temperatures, respectively, are reached. Assuming that initiation is quantitative, the general kinetic expression of propagation for the acid chloride–silver salt system is given by:

$$\ln\left(\frac{M_0-M_e}{M_t-M_e}\right)=k_pI_0t \qquad (4)$$

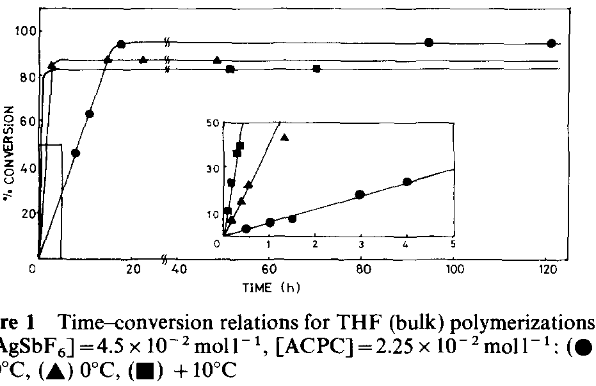


Figure 1 Time–conversion relations for THF (bulk) polymerizations, at $[AgSbF_6]=4.5\times10^{-2}$ mol l^{-1}, $[ACPC]=2.25\times10^{-2}$ mol l^{-1}: (●) -20°C, (▲) 0°C, (■) $+10$°C

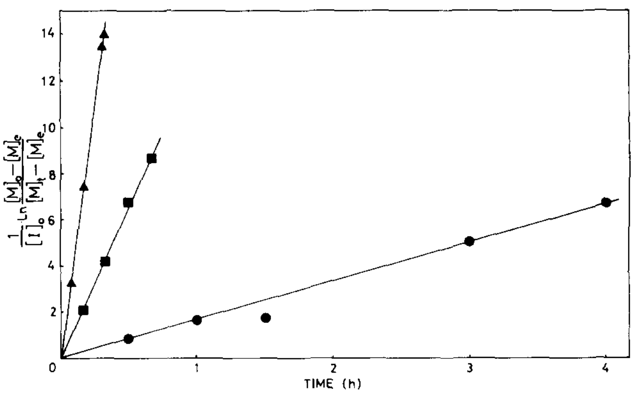


Figure 2 Kinetic results for the polymerization of THF (bulk): (●) -20°C, (■) 0°C, (▲) $+10$°C

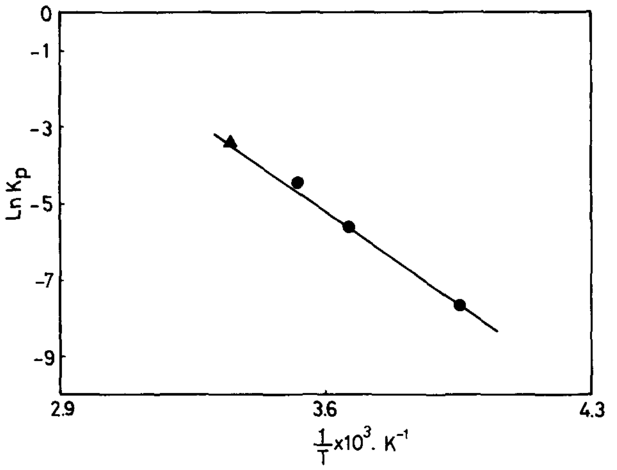


Figure 3 Arrhenius plot for the polymerization of THF (bulk): (●) this work, (▲) from ref. 9

In the present work, all measurements of equilibrium monomer concentrations M_e were performed gravimetrically. Kinetic results obtained for the three temperatures are illustrated in *Figure 2*. The straight lines obtained in all cases indicate the absence of termination reactions as observed by Franta *et al.*[9], who used mono- and multifunctional oxocarbenium salts in the polymerization of THF. The propagation rate constants were determined from the slopes of the straight lines as $k_p=4.7\times10^{-4}$ at -20°C, 3.7×10^{-3} at 0°C and 1.2×10^{-2} l mol^{-1} s^{-1} at $+10$°C. An Arrhenius plot (*Figure 3*) gives an activation energy of $E_a=57.6$ kJ mol^{-1}, which is in reasonable agreement with the reported values[10]. The equilibrium THF concentration is related to temperature by the equation[11]:

$$\ln[\mathrm{THF}]_{eq}=\frac{1}{T}\left(\frac{\Delta H_p}{R}\right)-\frac{\Delta S_p^\circ}{R} \qquad (5)$$

where ΔH_p is the heat of polymerization and ΔS_p° is the entropy change. *Figure 4* shows a plot of $\ln[\mathrm{THF}]_{eq}$ *versus* $1/T$. From this plot ΔH_p and ΔS_p° were estimated to be -24 kJ mol^{-1} and -86.7 J K^{-1} mol^{-1}, respectively. These values are also in good agreement with previous reports[12]. In this connection, it is interesting to note that the reported value[9] of $[\mathrm{THF}]_{eq}$ (3.1 mol l^{-1}) for the polymerization of THF initiated by $C_6H_5CO^+SbF_6^-$ at 25°C also fits with our values (see *Figure 4*), which implies that azo-oxocarbenium initiation shows the general behaviour of this type of initiation. When $AgBF_4$ was utilized in the system, a significant decrease in the rate of polymerization and broadening of the molecular-weight distribution were observed. Therefore, it seemed appropriate to use a silver salt with SbF_6^- counter-ion throughout this work. *Table 1* lists the monomer con-

Table 1 Polymerization of tetrahydrofuran (bulk)[a]

$AgSbF_6$ ($mol\,l^{-1}$)	ACPC ($mol\,l^{-1}$)	Conversion (%)	$[\eta]$ ($dl\,g^{-1}$)
9×10^{-2}	4.5×10^{-2}	44	0.74
5×10^{-2}	2.5×10^{-2}	28	1.10
1×10^{-2}	5.0×10^{-3}	5	2.12
5×10^{-3}	2.5×10^{-3}	3	2.17

[a] Reaction temp. 0°C; reaction time 80 min

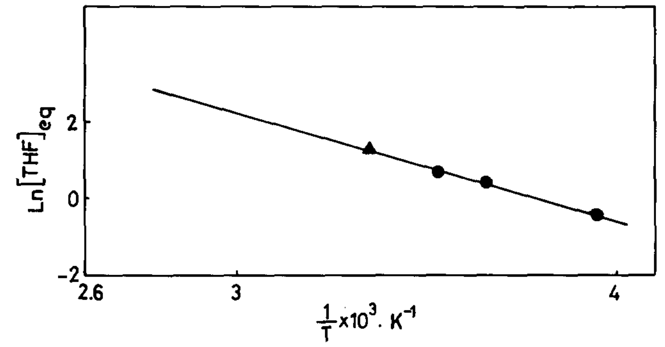


Figure 4 Equilibrium monomer concentration as a function of temperature: (●) this work, (▲) from ref. 9

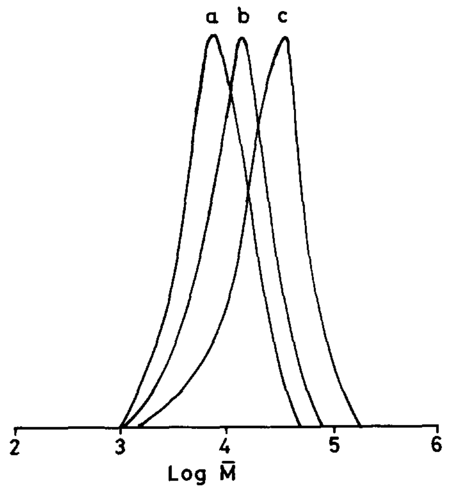


Figure 5 G.p.c. chromatograms of polytetrahydrofuran obtained at different reaction times: (a) 30 min, (b) 60 min, (c) 240 min. Reaction temperature −20°C

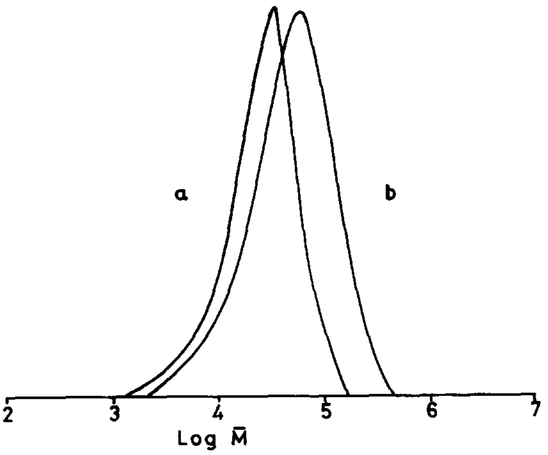
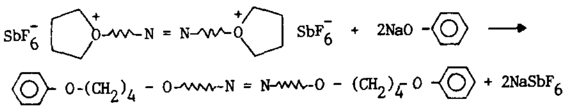


Figure 6 G.p.c. chromatograms of polytetrahydrofuran obtained at different temperatures: (a) −20°C, (b) +10°C

versions and viscosities at different initiator concentrations. They indicate that the monomer conversions and viscosities increased with increasing initiator concentration. *Figures 5* and *6* show the g.p.c. chromatograms of PTHF produced from the azo-oxocarbenium initiator at different polymerization times and temperatures, respectively. The figures indicate that the average molecular weight increases with both increasing reaction time and increasing temperature, and the molecular-weight distribution becomes broader.

Confirmation of the structures of the molecules formed was obtained from detailed characterization of PTHF end-capped with phenoxy groups. For this purpose polymerization of THF was initiated by $8\times10^{-2}\,mol\,l^{-1}$ ACPC and $1.6\times10^{-1}\,mol\,l^{-1}$ $AgSbF_6$ at 0°C. After 7 min, propagating chain ends were converted into phenyl ether by treatment with sodium phenoxide as described by Saegusa[13]:



(6)

The phenoxy end-groups exhibit a strong u.v. absorption at 272 nm in addition to the relatively weak absorption of the azo group at 350 nm. Knowing the extinction coefficients and assuming that each polymer chain contains two phenoxy and one azo groups, the value of $\bar{M}_n$ can be calculated. ^1H n.m.r. is another efficient method[14] of determining number-average molecular weights. The value for the sodium-phenoxide-deactivated sample was obtained from the peak areas of the aromatic protons (7.2 ppm) and of the methylene protons of PTHF chain (1.5 and 3.3 ppm). The data obtained on characterization of PTHF with phenoxy end-groups are collected in *Table 2*. As can be seen from these values, there is satisfactory agreement between the number-average molecular

Table 2 Number-average molecular weights of polytetrahydrofuran[a]

Method of determination	$\bar{M}_n$
Viscosity	3300[b]
U.v. (phenyl ether)	3600
U.v. (azo)	3550
^1H n.m.r.	3800

[a] For polymerization conditions see text

[b] Determined from the solution viscosity in benzene at 20°C using $[\eta]=2.59\times10^{-2}M^{0.82}$

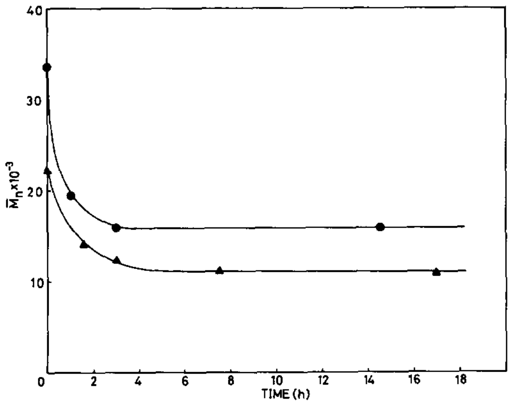


Figure 7 Decrease of number-average molecular weight with time of thermolysis at 60°C in benzene. $\bar{M}_{n0}=33\,700$ (●), 21 700 (▲)

Table 3 Thermolysis of polytetrahydrofuran at 60°C in benzene

$\bar{M}_{n0}$	$\bar{M}_{ni}$	N_s	Number of —N=N— per macromolecule
21 700	10 600	1.04	1.0
33 700	15 800	1.1	1.0

weights obtained by all methods. This clearly indicates that initiation proceeds by addition on to monomer, and polymer chains carry one azo linkage and two phenoxide functions per chain. Even more convincing evidence for the presence of the azo linkage was obtained from the thermal degradation of polymers produced by means of azo-oxocarbenium initiation. The thermolysis of the azo group was almost complete after 6 h heating at 60°C (*Figure 7*). *Table 3* summarizes the thermolysis data of two azo-linked PTHFs with different molecular weights; $\bar{M}_{n0}$ and $\bar{M}_{ni}$ indicate the number-average molecular weights before and after thermolysis. The agreement between the number of chain scissions per macromolecule, $N_s = (\bar{M}_{n0}/\bar{M}_{ni}) - 1$, and the expected azo content is remarkable.

CONCLUSIONS

As was shown earlier, block polymerization via cationic and radical routes provides a versatile two-stage method applicable to most nucleophilic and vinyl monomers. The overall structure of the block copolymer is determined by the well defined structure of the prepolymer, which itself requires knowledge of the reactivities of the components and of the reaction kinetics. Cationic 'living' polymerization techniques for THF can be used in the synthesis of well defined prepolymers. The azo functionality can be introduced efficiently, upon initiation, by using an azo-oxocarbenium salt as initiator. The block copolymerization of such prepolymers with various vinyl monomers is now under investigation and will be described in another paper.

REFERENCES

1 Riess, C., Hurtrez, G. and Bahadur, P. Block copolymers in 'Encyclopedia of Polymer Science and Engineering', 2nd Edn., Wiley, New York, 1985, Vol. 2
2 Verome, R., Fayt, R. and Quhadi, T. *Prog. Polym. Sci.* 1984, **10**, 87
3 Abadie, M. J. M. and Qurahmoune, D. *Br. Polym. J.* 1987, **19**, 247
4 Yağcı, Y. *Polym. Commun.* 1985, **26**, 7
5 Akar, A., Aydoğan, A. C., Talınlı, N. and Yağcı, Y. *Polym. Bull.* 1986, **15**, 293
6 Yağcı, Y. *Polym. Commun.* 1986, **27**, 21
7 Simionescu, C., Sik, K. G., Comanita, E. and Dumitru, S. *Eur. Polym. J.* 1984, **20**, 467
8 Kurata, M., Utiyama, H. and Kamada, K. *Makromol. Chem.* 1965, **88**, 281
9 Franta, E., Reibel, L., Lehmann, J. and Penczek, S. *J. Polym. Sci. Symp.* 1976, **56**, 139
10 Croucher, T. G. and Wetton, R. E. *Polymer* 1976, **17**, 205
11 Dainton, F. S. and Ivin, K. J. *Q. Rev.* 1958, **12**, 61
12 Dreyfuss, P. and Dreyfuss, M. P. *Adv. Polym. Sci.* 1967, **4**, 528
13 Saegusa, T. and Matsumoto, S. *J. Polym. Sci.* (*A-1*) 1968, **6**, 1559
14 Vargas, J. S., Zillox, J. G., Rempp, P. and Franta, E. *Polym. Bull.* 1980, **3**, 83