N-alkoxy pyridinium ion terminated polytetrahydrofurans. Synthesis and their use in photoinitiated block copolymerization

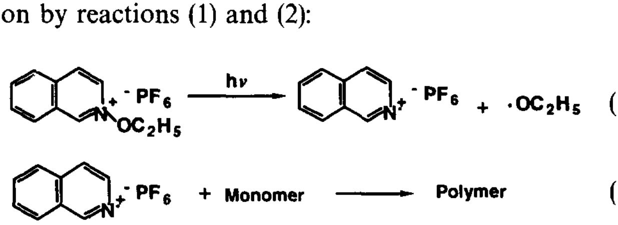
G. Hizal*, Y. Yağci* and W. Schnabel†
Hahn-Meitner-Institut Berlin GmbH, Glienicker Straße 100, D-14109 Berlin, Germany
(Received 1 December 1993; revised 7 March 1994)

Living polytetrahydrofuran was terminated with pyridinium or isoquinolinium N-oxide to yield polymers with the corresponding end groups. Direct and sensitized irradiation of these photoactive polytetrahydrofurans produced alkoxyl radicals at both chain ends capable of initiating the radical polymerization of methyl methacrylate. In this way, triblock copolymers were formed. The block copolymer composition was determined with the aid of g.p.c. and optical and ^{1}H n.m.r. spectroscopy.

(Keywords: living cationic polymerization; tetrahydrofuran; pyridinium ions)

INTRODUCTION

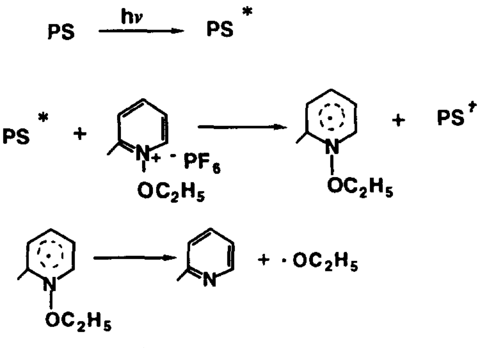
Living polymerization allows the preparation of various well-defined polymers with functional end groups. It has been shown that cyclic ethers such as tetrahydrofuran (THF) can be polymerized without chain transfer and termination reactions under closely controlled conditions[1-3]. The oxonium group of the living chain can react with nucleophiles and thus gives rise to a variety of functional groups[4-6]. Pyridinium salts are generally prepared by reacting N-oxides with triethyloxonium salts. Since the oxonium ion is the end group of living THF chains, N-alkoxy pyridinium ion terminated polymers can be obtained by quenching the living ends of the polymer with N-oxides. It has been shown that certain N-alkoxy pyridinium and N-alkoxy isoquinolinium ions are capable of acting as photoinitiators for the cationic polymerization[7-9]. A possible mechanism for the initiation of cationic polymerization applies to the photolytic generation of radical cations and ethoxyl radicals. This is illustrated for the case of the N-ethoxy isoquinolinium ion by reactions (1) and (2):



(1)

(2)

The decomposition of pyridinium ions also can be induced indirectly via the reaction with electronically excited sensitizers (PS).



(3)

(4)

(5)

PS: Photosensitizer

The alkoxyl radicals so generated can initiate the free radical polymerization of appropriate monomers[10]. Therefore, it seemed feasible to use polytetrahydrofurans (PTHFs), terminated by N-alkoxy pyridinium ions, as polymeric photoinitiators for the polymerization of monomers such as methyl methacrylate (MMA) that readily polymerize by a free radical mechanism. As will be shown below, block copolymers of THF and MMA, i.e. of monomers of quite different chemical nature, can be prepared by this method.

In the text, the polymers terminated by N-alkoxy-2-methyl pyridinium, N-alkoxy-4-phenyl pyridinium or N-alkoxy isoquinolinium ions are denoted by PTHF-MP, PTHF-PP and PTHF-IQ, respectively.

EXPERIMENTAL

Materials

THF was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. MMA (Aldrich) was passed through a column containing basic alumina (Type Brockmann 1) and distilled over CaH_2 *in vacuo*

---

*On leave from the Department of Chemistry, Istanbul Technical University, TR-80626 Istanbul, Turkey
†To whom correspondence should be addressed

0032-3861/94/20/4443-06

under argon. The N-oxides (2-picoline, isoquinoline and 4-phenyl pyridine) (Aldrich) were used as received. Triflic anhydride and triethyloxonium hexafluorophosphate (Aldrich) were used as received. Chloroform (E. Merck) was washed with water, dried with $CaCl_2$ and distilled over CaH_2. Dichloromethane (E. Merck) was treated with concentrated H_2SO_4, and washed with Na_2CO_3 solution (5%) and water. After drying with $CaCl_2$ it was refluxed and distilled over P_2O_5. Finally, it was stored over activated molecular sieve (type 4 Å).

Synthesis of pyridinium salts

N-ethoxy-2-methyl pyridinium hexafluorophosphate ($EMP^+PF_6^-$), N-ethoxy-4-phenyl pyridinium hexafluorophosphate ($EPP^+PF_6^-$) and N-ethoxy isoquinolium hexafluorophosphate ($EIQ^+PF_6^-$) were prepared according to a procedure described previously[7].

Synthesis of N-alkoxy pyridinium and N-alkoxy isoquinolinium ion terminated PTHFs

A three-necked flask equipped with an argon inlet and a rubber septum was connected to a vacuum line. The flask was dried at 130°C under vacuum. After cooling to room temperature, THF (50 ml) was distilled into the flask. The flask was then disconnected under argon and placed into a thermostatically controlled bath. The initiation of the polymerization was induced by adding triflic anhydride (0.104 ml, 0.62 mmol) under stirring at 25°C. After a given time an aliquot sample was removed for g.p.c. characterization by a syringe and the polymerization was terminated by the addition of methanol. The remaining part of the living PTHF was terminated by the addition of a solution of an N-oxide (12.3 mmol) in dichloromethane (CH_2Cl_2, 10 ml). The polymerization mixture was stirred for 15 min at 25°C, poured into methanol and cooled to −20°C. Finally, the precipitated polymer was filtered off and dried *in vacuo.*

Block copolymerizations

Block copolymerization of MMA using PTHF-MP. The polymer PTHF-MP (0.156 g) was dissolved in CH_2Cl_2 (2 ml). The solution was put into a Pyrex tube (i.d. 10 mm) and MMA (1.5 ml, 4 mol l^{-1}) and anthracene (0.0033 g) were added. The tube was degassed under high vacuum and sealed under argon prior to irradiation at 350 nm in a Rayonet reactor equipped with a rotating sample holder. Appropriate cut-off filters were placed in front of the tube.

Block copolymerization of MMA using PTHF-PP and PTHF-IQ. To a solution of CH_2Cl_2 (2 ml) containing a given amount of the polymer (PTHF-PP or PTHF-IQ), MMA (1.5 ml) was added. The tube was degassed under high vacuum and sealed under argon. Irradiations were carried out using a Rayonet photoreactor equipped with lamps which emitted light at nominally 350 nm.

Polymerization of MMA using $EMP^+PF_6^-$. The $EMP^+PF_6^-$ (0.011 g) was dissolved in CH_2Cl_2 (2 ml) and the same procedure was applied as for the block copolymerization of MMA using PTHF-MP.

Fractionation of block copolymers

After photolysis of the reaction mixtures, block copolymers were separated by precipitation in methanol at room temperature. By cooling the supernatant solution to −20°C and maintaining it at that temperature overnight a second polymer fraction precipitated. Both fractions were dried and characterized by g.p.c. and spectral analysis.

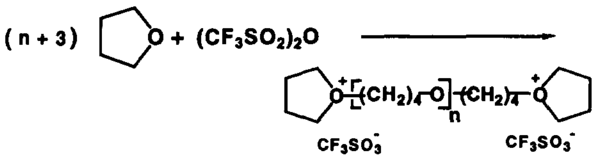
Analysis of polymers

I.r. spectra were recorded on a Biorad FTS-7 spectrophotometer using KBr discs. ^1H n.m.r. spectra were recorded on a Varian instrument (model EM 390) in $CDCl_3$ solution using tetramethylsilane as the internal standard. U.v.-vis. spectra were recorded on a Shimadzu spectrophotometer (model 2101PC) in CH_2Cl_2 solutions. G.p.c. analyses were performed with a set-up consisting of a Shimadzu pump (model LC6A) and four Ultrastyragel columns with porosities 10^5, 10^4, 10^3, and 500 Å, respectively. THF was used as eluent at a flow rate of 1 ml min^{-1} and detection was carried out with a Waters differential refractometer (model 410). Samples were injected by using a 20 μl sample loop. Concentrations were normally in the range of 2–3% w/v. Molecular weights were calculated with the aid of polystyrene standards.

RESULTS AND DISCUSSION

Preparation and characterization of PTHFs having terminal N-alkoxy pyridinium ions

PTHF terminated by N-alkoxy pyridinium ions was prepared by the living polymerization of THF using triflic anhydride as bifunctional initiator[2,3] at 25°C according to reaction (6):



(6)

Table 1 Preparation and characterization of N-alkoxy pyridinium ion terminated PTHF

	Polymerization time (min)	Conversion (%)	$M_{\text{calc.}}$[a]	M_n[b]	M_n[c]	M_n[d]	M_w/M_n[e]
PTHF-MP	25	12	8700	8400	7900	8300	1.10
PTHF-IQ	25	12	8700	8400	8300	8100	1.10
PTHF-PP	20	9	6600	6600	6500	6100	1.17

[THF] = 12.3 mol^{-1} (bulk), [In] = 1.23×10^{-2} mol l^{-1}, temperature = 25°C

[a] $M_{\text{calc.}} = \Delta m/[\text{In}] \times 72$

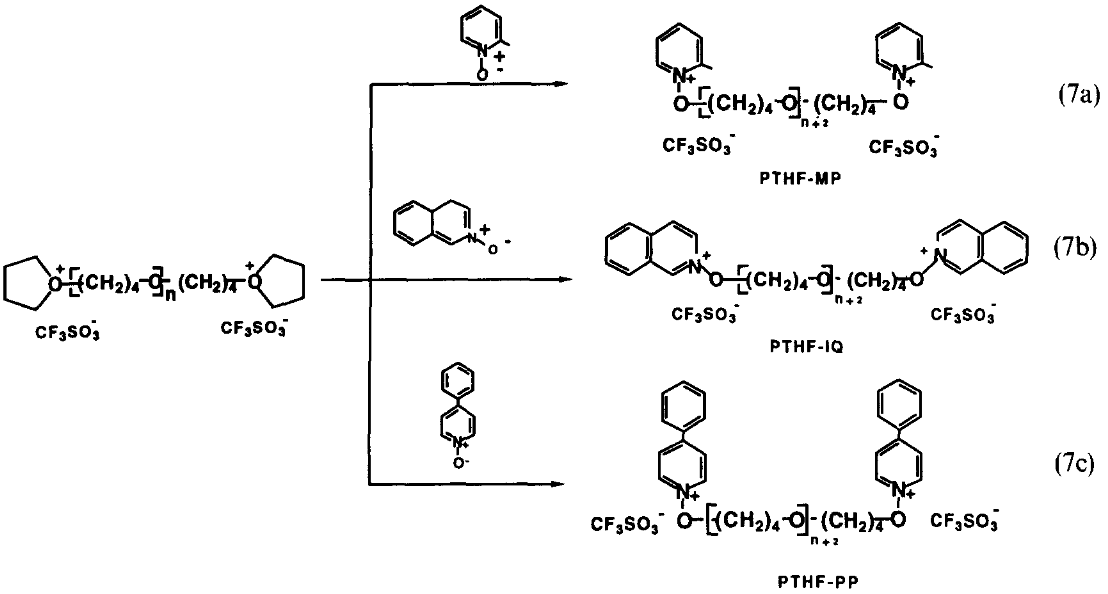
[b] Obtained by g.p.c.; molecular weight of end groups has been subtracted

[c] Determined by u.v. measurement

[d] Determined by ^1H n.m.r. comparing the content of the aromatic protons and the $-OCH_2-$ protons of PTHF

[e] Obtained by g.p.c. based on the calibration with polystyrene standards

The living propagating chain readily reacts with N-oxides according to reactions (7a)–(7c):



The structure of PTHFs terminated at both ends by N-alkoxy pyridinium ions was confirmed by ^1H n.m.r., u.v.-vis. and g.p.c. analysis. The results are summarized in *Table 1*. In the case of the living polymerization of THF, the molecular weight of the polymer is calculated by:

$$M_{\text{calc.}} = \frac{\Delta m}{[\text{In}]} \times 72 \qquad (8)$$

where Δm (mol l^{-1}) is the amount of monomer consumed and [In] (mol l^{-1}) is the initiator concentration. As can be seen from *Table 1* there is good agreement between the molecular weight values determined by g.p.c. and the calculated values. The ^1H n.m.r. spectrum of a typical PTHF-PP sample (*Figure 1*) exhibits signals in the range of 7–9 ppm corresponding to the aromatic protons of the 4–phenyl pyridine ring in addition to signals characteristic for PTHF. Similar ^1H n.m.r. spectra were observed for the other polymers (PTHF-MP and PTHF-IQ). Based upon a comparison of the ratio of aromatic protons to $-OCH_2-$ protons of PTHFs, the molecular weights of the polymers were calculated. The structure of the polymers was assigned by means of u.v. spectral measurement. The u.v. spectra of the polymers show absorption bands characteristic of those of the corresponding low molecular weight pyridinium ions. This can be seen in *Figure 2* where optical absorption spectra of PTHF-PP and $EPP^+PF_6^-$ are presented. Using the values of the extinction coefficient of the low molecular weight pyridinium ions given in *Table 2*, the molecular weights of the polymers were calculated. The, remarkable agreement of the values obtained by the different methods shows that quantitative functionalization was achieved in all cases. *Figure 3* shows a g.p.c. trace (B) obtained from a polymer prepared by adding a 10-fold excess of 2-methyl pyridinium N-oxide to a batch of living PTHF at 25°C 25 min after the initiation. The mixture was allowed to stand for a further 15 min at that temperature before precipitation by the addition of excess methanol. *Figure 3* also shows a g.p.c. trace (A) of a sample obtained by PTHF termination with excess methanol. It may be noted that the maximum position of the PTHF-MP chromatogram corresponds to a longer retention time than that of the methanol-terminated polymer. An asymmetric signal and a relatively long retention time have been found for a PTHF sample containing quarternary ammonium groups by Cunliffe *et al.*[4]. The g.p.c. behaviour of PTHF samples having ionic end groups has been explained in terms of specific interactions of the terminal ionic groups with polar ligands on the cross-linked polystyrene matrix.

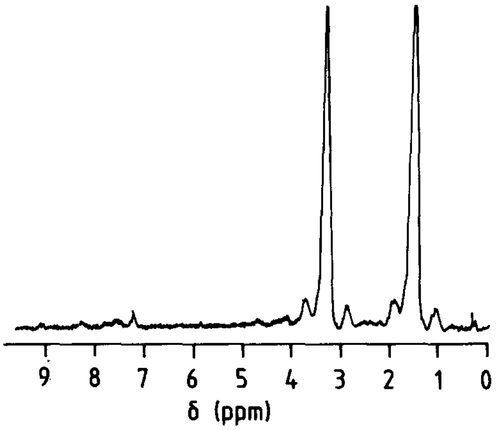


Figure 1 ^1H n.m.r. spectrum of PTHF terminated by N-alkoxy 4-phenyl pyridinium ions

Preparation and characterization of block copolymers

According to the absorption characteristics of PTHF-MP, PTHF-PP and PTHF-IQ two different methods were involved in order to transform these polymers into block copolymers containing MMA. PTHF-PP and PTHF-IQ absorb light at relatively long wavelengths, i.e. at 300–350 nm. Upon direct irradiation at these wavelengths polymeric alkoxyl radicals are produced, as

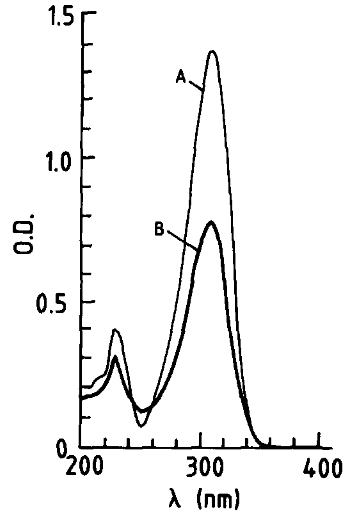


Figure 2 Absorption spectra of CH_2Cl_2 solutions of (A) $EPP^+PF_6^-$ (6.4×10^{-5} mol l^{-1}) and (B) PTHF-PP (3.6×10^{-5} mol l^{-1})

Table 2 Extinction coefficient values of low molecular weight pyridinium ions

Pyridinium ion	λ_{max}(nm)	ε(l mol^{-1} cm^{-1})
$EMP^+PF_6^-$	266	5925
$EIQ^+PF_6^-$	337	4218
$EPP^+PF_6^-$	310	21440

Solvent: dichloromethane

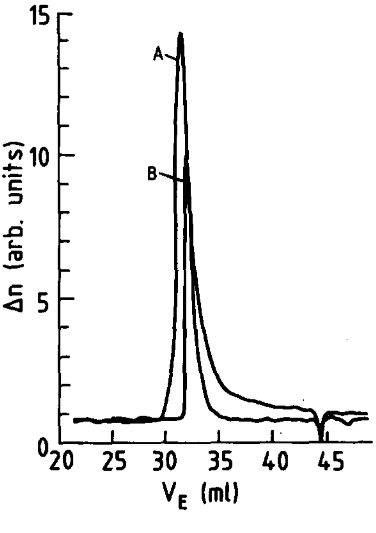
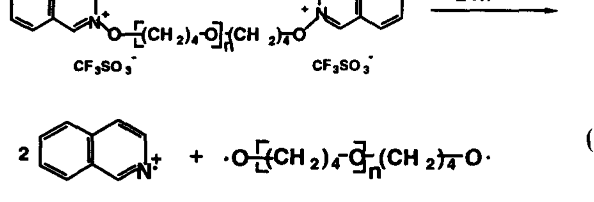


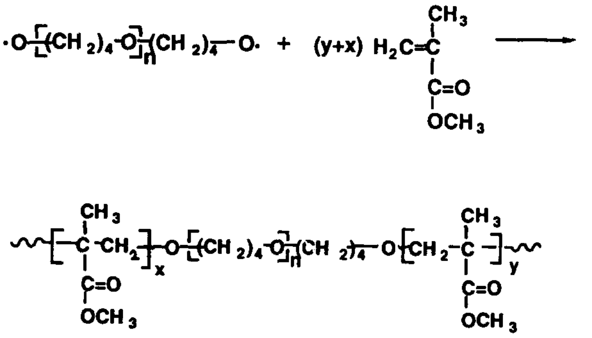
Figure 3 G.p.c. traces of (A) PTHF (terminated by methanol) and (B) PTHF-MP terminated by 2-methyl pyridine N-oxide

shown in reaction (9) for the case of PTHF-IQ:



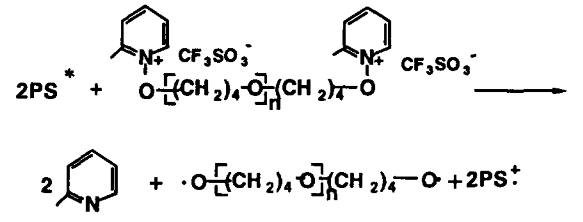
(9)

When reaction (9) is performed in the presence of a monomer polymerizable by a free radical mechanism, such as MMA, a block copolymer is formed:



(10)

As has been shown earlier for a low molecular weight analogue[10], the spectral sensitivity of PTHF-MP may be extended to longer wavelengths with the aid of certain sensitizers. Indeed, upon irradiation of a solution containing anthracene and PTHF-MP macroradicals are formed via electron transfer from the electronically excited sensitizer (PS) to the terminal pyridinium ions:



(11)

In the presence of a monomer polymerizable by a free radical mechanism, block copolymer formation would be initiated as in the case of direct irradiation. Results typical for both direct and sensitized block copolymer formation are summarized in *Table 3*. For the sake of comparison the polymerization of MMA was also initiated under similar reaction conditions with the aid of the system $EMP^+PF_6^-$/anthracene. Notably, MMA was converted to a similar extent in both cases (runs 1 and 4 in *Table 3*). However, the molar mass of the PMMA segments in the block copolymer ($\sim 9 \times 10^4$) is much higher than that of the homopolymer ($\sim 2 \times 10^4$). This difference might reflect the bifunctional nature of the initiating species in

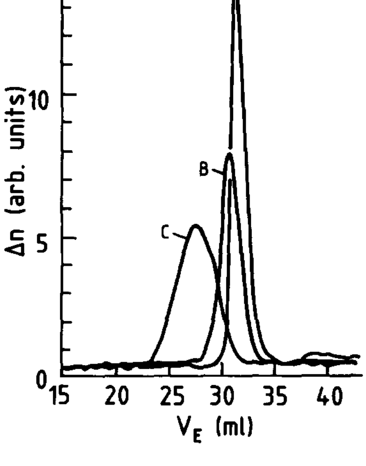


Figure 4 G.p.c. traces of (A) PTHF (terminated by methanol) and block copolymer obtained from PTHF-MP and precipitated with methanol at (B) −20°C and (C) room temperature

Table 3 Preparation and characterization of THF-MMA block copolymers

Run	Initial polymer ($M_n \times 10^{-3}$)	Initiator conc. $\times 10^2$ (mol l^{-1})	Anthracene (mol l^{-1})	Polymerization time (h)	Conversion (%)	Fractions (%)[d] ($M_n \times 10^{-3}$)	
						Room temperature	-20°C
1[a]	PTHF-MP (8.4)	1.06	0.053	4	12	89 (90)	11 (25)
2[b]	PTHF-PP (6.6)	3.50	–	14	53	74 (63.5)	26 (26)
3[b]	PTHF-IQ (8.4)	1.40	–	14	35	62 (59)	38 (22.7)
4[c]	–	1.06	0.053	4	28	100 (20.2)	–

[MMA] = 4 mol l^{-1} in dichloromethane

[a] Irradiated in a Rayonet photoreactor using 350 nm lamps and a cut-off filter (Schott WG 345)

[b] Irradiated in a Rayonet photoreactor using 350 nm lamps (no filter)

[c] Homo PMMA obtained with the aid of the system EMP$^+$PF$_6^-$/anthracene at $\lambda_{inc} > 345$ nm using a cut-off filter (Schott WG 345)

[d] Percentage of polymeric product precipitated from methanol

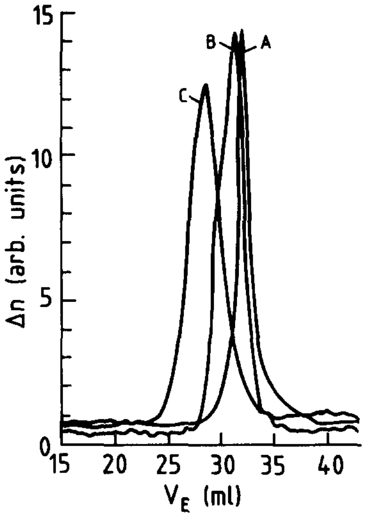


Figure 5 G.p.c. traces of (A) PTHF (terminated by methanol) and block copolymer obtained from PTHF-IQ and precipitated from methanol solution at (B) -20°C and (C) room temperature

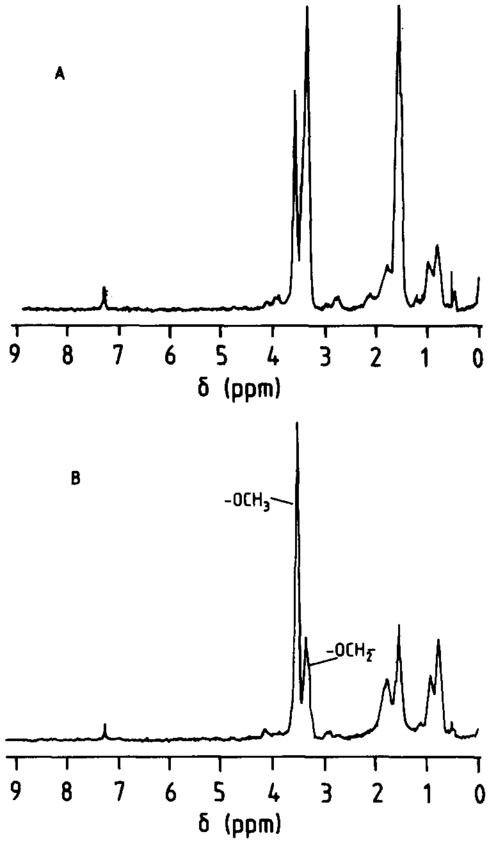


Figure 6 ^{1}H n.m.r. spectra of block copolymers obtained from PTHF-MP and precipitated with methanol at (A) -20°C and (B) room temperature

the case of run 1, which leads to the formation of long chains (chain growth at both ends of the initiator molecules). Moreover, combination which occurs to some extent will lead to longer macromolecules than in the case of polymerizations started by monofunctional initiators (run 4). The precursor PTHFs dissolve in methanol at room temperature and precipitate at low temperature, i.e. -20°C. The temperature-dependent solubility behaviour of low molecular weight PTHFs makes it possible to fractionate resulting block copolymers with different MMA segment lengths. *Figure 4* shows g.p.c. traces of the initial PTHF-MP and of block copolymer fractions precipitated at room temperature and at -20°C. It is interesting to note that the fractions do not contain residual initiating polymer. This was corroborated by recording the u.v. absorption spectra of the two polymer fractions. These spectra no longer contain the strong absorption band ($\lambda_{max} \approx 310$ nm) of the pyridinium end groups indicating their complete conversion. Obviously, the polymer fraction precipitating at -20°C consists of a copolymer with short MMA segments. Similar observations were made in the case of block copolymers produced by direct irradiation (*Figure 5*). These findings were further supported by ^{1}H n.m.r. analyses of the block copolymers obtained after fractionation. From a comparison of the ^{1}H n.m.r. spectra in *Figures 6A* and *B* it can be seen that as the length of the MMA segments in the block copolymer increases the signal corresponding to protons in the -OCH$_3$ groups at 3.6 ppm increases relative to that of the protons in the -OCH$_2$- groups in PTHF at 3.4 ppm. The composition of the block copolymers was also analysed by i.r. measurements. The i.r. spectra of the block copolymers display the characteristic carbonyl band at 1730 cm^{-1} and the ether band at 1100 cm^{-1} indicating the existence of both THF and MMA segments. Assuming that the radical polymerization of MMA is mainly terminated by disproportionation and PTHF-MP, PTHF-PP and PTHF-IQ act as bifunctional initiators, the resultant block copolymers are expected to be mainly of the ABA type.

In conclusion, this work demonstrates that 'polymeric' pyridinium ions may be prepared by taking advantage of the living polymerization of THF and quantitative quenching of the living ends by N-oxides. The photoinitiating capability of these polymers provides a versatile method for preparing block copolymers which cannot be obtained by conventional methods.

ACKNOWLEDGEMENT

One of the authors (G.H.) wishes to express his sincere gratitude to the Alexander von Humboldt-Stiftung for financial support.

REFERENCES

1 Croucher, T. G. and Wetton, R. E. *Polymer* 1976, **17**, 205
2 Smith, S. and Hublin, A. J. *J. Macromol. Sci. Chem.* 1973, **A7**, 1399
3 D' Haese, F. and Goethals, E. J. *Br. Polym. J.* 1988, **20**, 103
4 Cunliffe, A. V., Hartley, D. B., Kingston, S. B., Richards, D. H. and Thompson, D. *Polymer* 1981, **22**, 101
5 Tezuka, Y. and Goethals, E. J. *Eur. Polym. J.* 1982, **18**, 991
6 Kobayashi, S., Uyama, H., Ogaki, M., Yoshida, T. and Saegusa, T. *Macromolecules* 1989, **22**, 4412
7 Yağci, Y., Kornowski, A. and Schnabel, W. *J. Polym. Sci., Polym. Chem. Edn* 1992, **30**, 1987
8 Böttcher, A., Hasebe, K., Hizal, G., Stellberg, P., Yağci, Y. and Schnabel, W. *Polymer* 1989, **22**, 2289
9 Yağci, Y., Lukaç, I. and Schnabel, W. *Polymer* 1993, **34**, 1130
10 Kayaman, N., Önen, A., Yağci, Y. and Schnabel, W. *Polym. Bull.* 1994, **32**, 589