

## Photo-induced Living Cationic Polymerization of Tetrahydrofuran. III. Synthesis of Poly(THF-co-3-MTHF)

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**Abstract :** Poly(3-methyltetrahydrofuran)(3-MTHF) and poly(tetrahydrofuran-co-3-MTHF), having very narrow molecular weight distribution were successfully synthesized via photo-induced living cationic polymerization in the presence of diphenyliodonium hexafluorophosphate. Linear relationship between % conversion and number average molecular weight of resulting poly(3-MTHF) in the polymerization of 3-MTHF, carried out at -22°C, indicates that the 5-membered cyclic oxonium ion, being responsible for the cationic propagation is stabilized by ion pair formation with hexafluorophosphate anion, supplied from the salt. The linear relationship between two parameters, mentioned above was also observed in the copolymerization of 3-MTHF with THF, carried out at 0 and -22°C. The molecular structures including the copolymer composition and average molecular weight and its distribution is determined by reaction parameters such as monomer feed ratio and reaction temperature.

### Introduction

In earlier articles[1,2], we have reported that a photo-induced living cationic poly(tetrahydrofuran (THF)) can be realized in the presence of diphenyliodonium hexafluorophosphate, a well known cationic initiator[3,4]. It was concluded that the living nature of the system was ascribed to the stabilization of five-membered cyclic oxonium ion, responsible for the cationic propagation, by the formation of ion pair with a less nucleophilic complex metalhalide anion, hexafluorophosphate, supplied from the initiator. Attempts have been made, therefrom, to synthesize poly(THF) based diblock copolymer by the sequential monomer addition method[1] and a four armed star shaped poly(THF) in the presence of pentaerythritol tetrakis (3,4-epoxybutanoate)[2].

Although much attention has been given to the potential utility of the living nature of cationic poly(THF) for the synthesis of various poly(THF) of well defined structures, such as terminally functional poly(THF)[5], block[6-8] and graft copolymers[9], any trial for the synthesis of poly(THF-co-3-methyl tetrahydrofuran) via photo-induced living cationic polymerization is not yet known.

In this article, we report the polymerization of 3-MTHF and copolymerization of 3-MTHF with THF via photo-induced living cationic polymerization in the presence of the salt in order to obtain a telechelic polyether diol, a starting material of polyurthane

synthesis.

### Experimental

#### Materials

Monomers, THF (Dongyang Chemicals) and 3-MTHF (Tokyo Kasei) were strictly dried on CaH<sub>2</sub> on vacuum line just before use after purification by conventional fractionation on LiAlH<sub>4</sub>. Diphenyliodonium hexafluorophosphate (Tokyo Kasei) was used without further purification as a photocationic initiator.

#### Photopolymerization

Necessary amount of monomers was introduced into pyrex ampoule by trap to trap distillation on high vacuum line where dried photocationic initiator was placed and sealed after repeated degassing by freeze-thaw technique. Polymerization samples were irradiated with 500 W high pressure mercury lamp (Ushio UI-501-C) at ambient temperature or 0°C, followed by dark reaction at 4°C, 0°C and -22°C for further reaction. After completion of the reaction, ampoule was opened and polymer was precipitated in excess methanol. % Conversion was determined by gravimetry.

#### Analysis

The molecular structure of the copolymer was identified by JEOL PMX 60SI <sup>1</sup>H NMR spectrometer using CCl<sub>4</sub> as a solvent. Molecular weight of the polymers was determined by GPC (Spectra Physics SP 8430 RI detector) using THF as a solvent (flow rate: 1 ml/min, column: 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup> Å in series).

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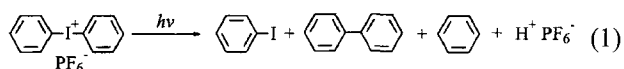
## Results and Discussion

### Photo-induced polymerization of 3-MTHF

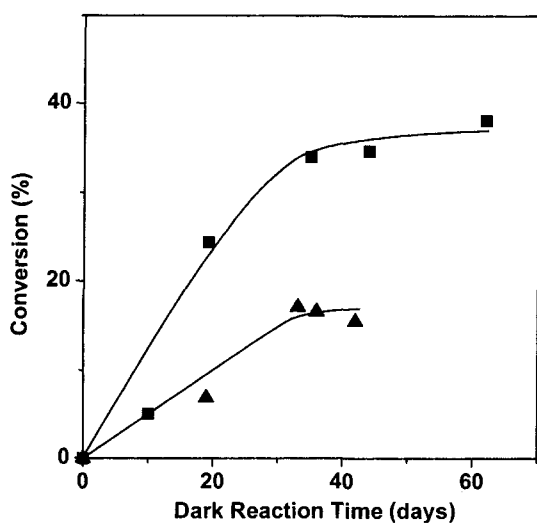
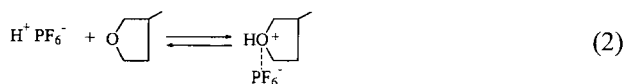
Figure 1 shows time-conversion curves of 3-MTHF polymerization carried out at 0 and -22°C, respectively, which reveals that the polymerization at 0°C proceeds with a very low rate to give 17% conversion for 17 days reaction period. It is believed that the polymerization in the irradiation (10 min) is negligible. Both curves carried out at 0 and -22°C are leveled off since an equilibrium is established between propagation and depropagation in this systems[1], i.e., 17% at 0°C and 35% at -22°C. Not only higher leveled off value at lower temperature but also much higher rate of polymerization is observed at -22°C than that carried out at 0°C. Actually, no polymer was obtained from the system, carried out at 4°C for 60 days, a reported value as the ceiling temperature of 3-MTHF[10].

Therefore, it is believed that the cationic polymerization of 3-MTHF proceeds successively by the nucleophilic attack of the monomer to the cyclic oxonium ion which is located at the growing polymer chain end which is a product of the protonation of five member cyclic ether, a photolytic product of the salt[3,4] as shown below.

Generation of protonic acid by photolysis of the salt



Initiation by protonation of 3-MTHF

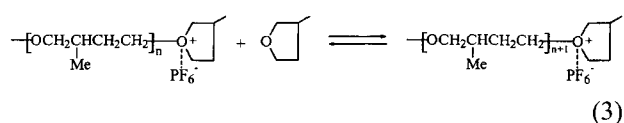


**Figure 1.** Time-conversion curves of photo-induced cationic polymerization of 3-MTHF in the presence of 0.05 M initiator, carried out in the dark at various temperature after photo-irradiation at room temperature for 10 min. ■ : -22°C, ▲ : 0°C.

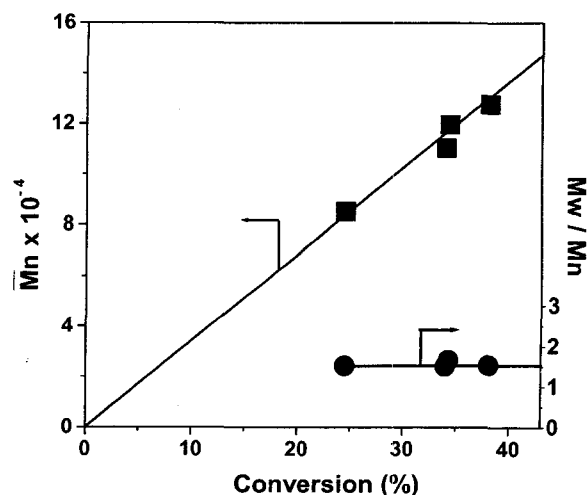
And the living nature of the cationic polymer system is due to the stabilization of the cationic propagating chain end by ion pair formation with less nucleophilic hexafluorophosphate anion, supplied from the salt, as shown in (2).

In such living system, namely, in the absence of the termination and chain transfer processes, an equilibrium is established between cationic propagation and depropagation. Accordingly, propagation is favored to depropagation due to exothermic nature of the polymerization of 3-MTHF as the temperature is lowered[10].

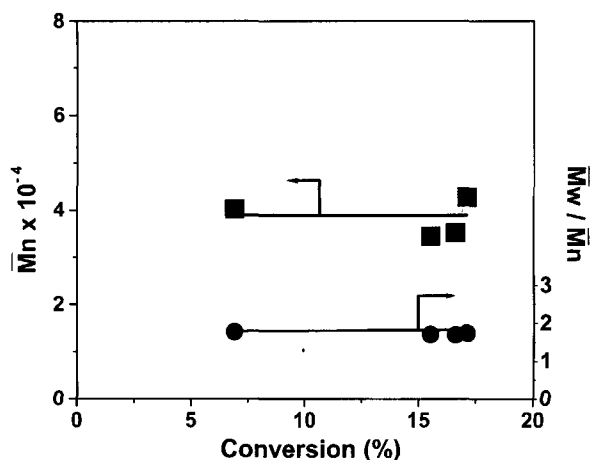
Equilibrium between propagation and depropagation



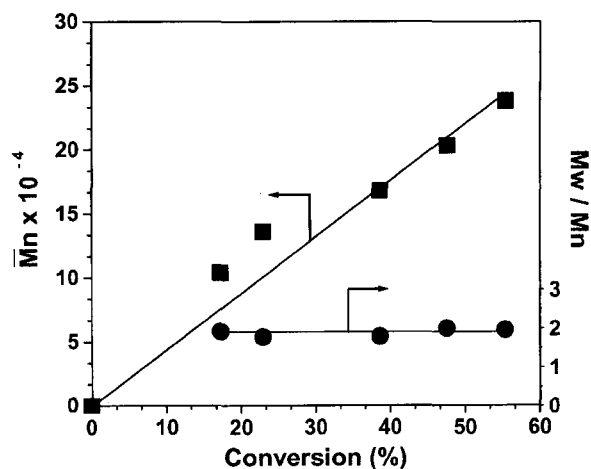
The relationship between number average molecular weight of resulting polymer and % conversion is shown in Figures 2 and 3. The linear relationship between % conversion and the number average molecular weight of resulting polymer at -22°C indicates that a living polymer, i.e., the absence of termination or chain transfer, is formed in this polymerization system and the polymer has narrow molecular weight distribution whose dispersity index is around 1.5, meaning that the rate of initiation is much higher than that of propagation. Meanwhile, the living nature of the cationic polymer at 0°C is not obvious, i.e., the relationship between number average molecular weight and % conversion deviates from the linearity and the dispersity index shows values scattered around 1.9.



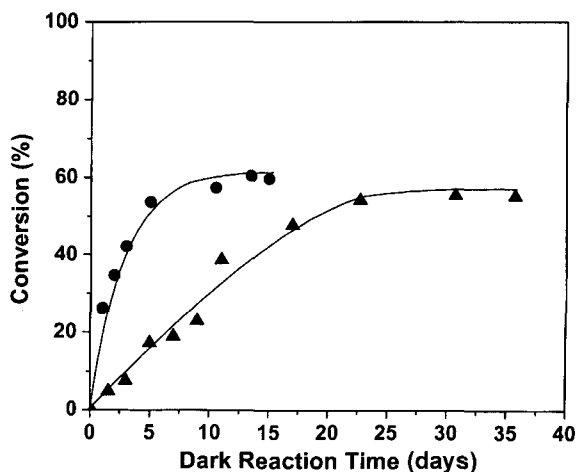
**Figure 2.** Dependence of number average molecular weight ( $M_n$ ) and its molecular weight distribution ( $M_w/M_n$ ) on % conversion in photo-induced cationic polymerization of 3-MTHF in the presence of 0.05 M initiator, carried out in the dark at -22°C after photoirradiation at room temperature for 10 min.



**Figure 3.** % Dependence of number average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of resulting polymer on % conversion in photo-induced cationic polymerization of 3-MTHF in the presence of 0.05 M initiator, carried out in the dark at 0°C after photoirradiation at room temperature for 10 min.



**Figure 5.** % Number average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of resulting polymer as a function of % conversion in photo-induced cationic copolymerization of 3-MTHF with THF in the presence of 0.05 M initiator, carried out in dark at -22°C after photoirradiation at 0°C for 10 min. THF:3-MTHF = 1:1 (v/v).



**Figure 4.** Time-conversion curves of photo-induced cationic copolymerization of 3-MTHF with THF in the presence of 0.05 M initiator, carried out in the dark at various temperatures after photoirradiation at 0°C for 10 min. THF:3-MTHF = 1:1 using volume ratio. ● : 0°C, ▲ : -22°C.

### Photo-induced copolymerization of 3-MTHF with THF

Figure 4 shows time conversion curves of the copolymerization of 3-MTHF with THF, carried out at 0 and -22°C. The monomer feed ratio is fixed at 1:1 (v/v). The conditions and procedures for the photoirradiation and polymerization are quite same with those, described in the polymerization of 3-MTHF. As same in the case of homopolymerization of 3-MTHF, both curves, carried out

at 0 and -22°C are leveled off after they reached their final % conversion values. It is evident from Figure 4 that the value of final conversion is independent on the reaction temperature but is a function of the monomer feed ratio. However, the rate of polymerization at 0°C is higher than that carried out at -22°C, which is strikingly different from the homopolymerization of 3-MTHF. This might be attributed to higher rate of initiation of THF. It has been reported that the rate of initiation of 3-MTHF at 0°C is very low because the ceiling temperature of 3-MTHF polymerization is located at 4°C.

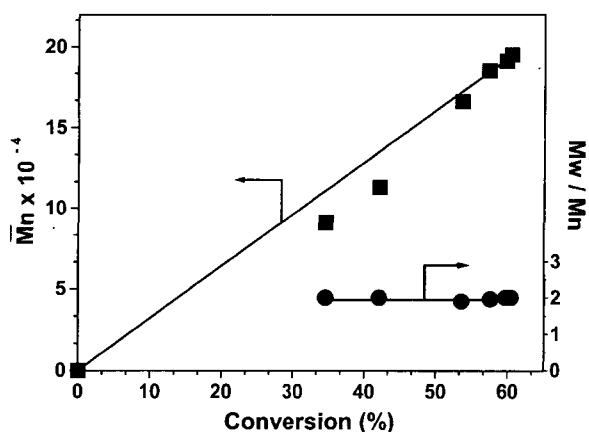
Figure 5 shows the relationship between % conversion and the number average molecular weight of resulting copolymer, photo-induced cationic copolymerization of 3-MTHF with THF (v/v=1/1), carried out at -22°C. The linear relationship between two parameters reveals the living nature of the copolymer and the dispersity index of the copolymer (around 1.9) is slightly larger than that of homopolymerization of 3-MTHF.

The result of the copolymerization, carried out at 0°C is shown in Figure 6, revealing that living nature becomes more remarkable when compared with that of homopolymerization of 3-MTHF, carried out at same temperature, however, the molecular weight distributions become wider in copolymerizations having a values around 2.

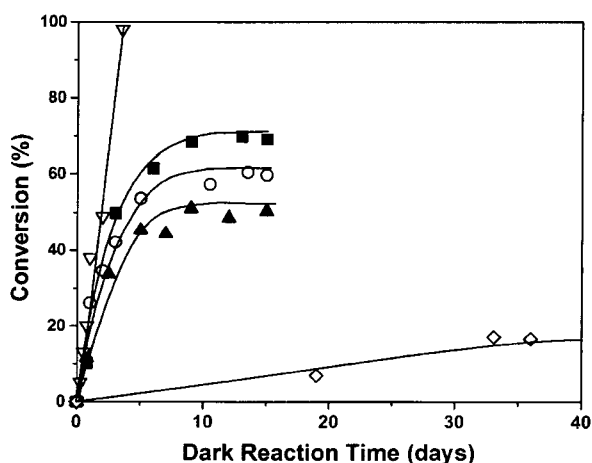
Time-conversion curves of the copolymerization, carried out at 0°C, under various monomer feed ratios, are shown in Figure 7. Our earlier data of THF homopolymerization[1] is also shown in the figure for the sake of comparison. As shown in the figure, the increase in the content of 3-MTHF in monomer feed results in not

only decrease in the rate of polymerization, but also decrease in the values final conversion %. The final % conversion value of THF-3-MTHF copolymerization gradually reduces to 70, 60, 50 and 17% as the mole fraction of 3-MTHF in monomer feed increases to 0.33, 0.5, 0.66, and 1, meanwhile that of THF homopolymerization showed a value of 98%[1].

The compositions of the copolymers were analyzed by means of  $^1\text{H-NMR}$ . A typical  $^1\text{H-NMR}$  spectrum of a copolymer is shown in Figure 8 and the compositions of



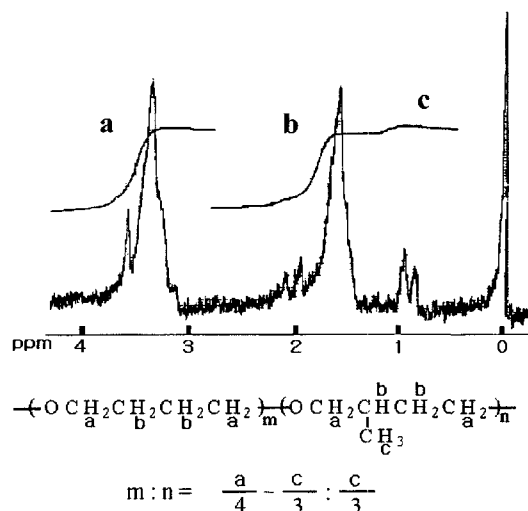
**Figure 6.** Number average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of resulting polymer in photo-induced cationic copolymerization of 3-MTHF with THF in the presence of 0.05 M initiator, carried out in the dark at  $0^\circ\text{C}$  after photoirradiation at  $0^\circ\text{C}$  for 10 min. THF:3-MTHF = 1:1 (v/v).



**Figure 7.** Time-conversion curves of photo-induced cationic copolymerization of 3-MTHF with THF in the presence of 0.05 M initiator, carried out in the dark at  $0^\circ\text{C}$  after photoirradiation at  $0^\circ\text{C}$  for 10 min. THF:3-MTHF =  $\nabla$  1:0,  $\blacksquare$  1:0.5,  $\circ$  1:1,  $\blacktriangle$  1:2,  $\diamond$  0:1 (v/v).

copolymers were estimated by the ratio of the area of proton signal, as designated in the figure. The results are summarized in Table 1.

Table 1 clearly shows that the content of 3-MTHF in the copolymer increases as the content of 3-MTHF increases in the monomer feed, and the average molecular weight of resulting copolymers increases as % conversion



**Figure 8.** An typical example of  $^1\text{H-NMR}$  spectrum of poly (RHF-3-MTHF). Photo-initiated polymerization in the presence of 0.05 M initiator  $0^\circ\text{C}$  for 10 min was carried out in the dark at  $0^\circ\text{C}$  for 3 days. Monomer feed ratio : THF:3-MTHF = 1:0.5 (v/v). Copolymer composition : THF:3-MTHF = 86:14.

**Table 1.** Results obtained by copolymerization of 3-MTHF with THF<sup>a</sup>

THF : MTHF <sup>b</sup>	Temp. ( $^\circ\text{C}$ )	Time (days)	Conv. (%)	$M_n^c$	$M_w/M_n^c$	$m:n^d$
1:1	-22	1.5	4.9	.	.	.
		3	7.6	.	.	.
		5	17.2	104000	1.92	.
		7	18.9	.	.	.
		9	22.9	136000	1.78	73:27
		11	38.6	168000	1.79	73:27
		17	47.6	203000	2.0	72:28
		22.7	54.1	224000	2.0	73:27
		30.7	55.4	238000	1.96	73:27
		35.7	55.1	231000	1.98	72:28
1:1	0	1	26.1	.	.	.
		2	34.6	91000	2.0	59:41
		3	42.1	113000	2.0	56:44
		5	53.6	165000	1.9	59:41
		7.6	62.4	200000	1.95	56:44
		10.5	57.3	185000	1.96	60:40
		13.5	60.4	195000	2.0	61:39
		15	59.7	191000	2.0	60:40

Table 1. Continued

THF : MTHF <sup>b</sup>	Temp. (°C)	Time (days)	Conv. (%)	$M_n^c$	$M_w/M_n^c$	m : n <sup>d</sup>
1:2	0	0.75	11.6	·	·	·
		2.5	33.7	125000	1.81	69:31
		5	45.5	161000	1.87	64:36
		7	44.4	173000	1.95	65:35
		9	51.1	133000	1.94	60:40
		12	48.6	187000	1.92	68:32
1:0.5	0	15	50.4	183000	1.96	65:35
		0.75	10.2	·	·	·
		3	49.9	249000	1.99	86:14
		6	61.5	279000	2.1	90:10
		13	69.9	295000	1.98	88:12
		15	69.1	293000	1.97	89:11

a. [I] : 0.05 M ; Irradiation conditions : 0, 10 min.

b. Volume ratio.

c. Estimated by GPC.

d. Determined by <sup>1</sup>H NMR spectra; m: p(THF), n: p(MTHF).

increase and the composition of copolymers is almost independent on the % conversion when monomer feed ratio and the temperature are fixed. Copolymers obtained from 0°C under 1:1 (THF:3-MTHF) monomer feed ratio have almost constant values (copolymer composition around 7/3 (THF/3-MTHF)) in the course of the polymerization, irrespective to the % conversion. The dispersity indices of the copolymers have values around 2 that are slightly larger than those of homopolymers.

### Conclusions

Poly(3-MTHF) and poly(THF-co-3-MTHF) having controlled molecular weight, relatively narrow distribution and copolymer compositions, have been successfully synthesized via photo-induced living cationic polymer-

ization mechanism. It was found that the living nature of the polymerization system is due to the stabilization of 5-membered cyclic oxonium ion, cationic propagating species by ion pair formation with hexafluorophosphate anion. The absence of termination and chain transfer process makes it possible to control of copolymer composition and molecular weight of copolymer by simple adjustment of some reaction parameters such as monomer feed ratio and reaction temperature.

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### References

1. S. Mah, D. You, H. Cho, S. Choi, and J. Shin, *J. Appl. Polym. Sci.*, **69**, 611 (1998).
2. S. Mah, H. Hwang, and J. Shin, *J. Appl. Polym. Sci.*, **74**, 2637 (1999).
3. J. V. Crivello and J. H. W. Lam, *J. Polym. Sci. Symp.*, **56**, 383 (1976).
4. J. V. Crivello and J. H. W. Lam, *Macromolecules*, **10**, 1307 (1977).
5. M. P. Dreyfuss and J. P. Kennedy, *J. Polym. Sci. Lett. Ed.*, **14**, 139 (1976).
6. J. L. Lambert and J. Goethals, *Makromol. Chem.*, **133**, 289 (1970).
7. Y. Yamashita and K. Chiba, *Polym. J.*, **4**, 200 (1973).
8. D. H. Richards, S. B. Kingstone, and T. Souel, *Polymer*, **19**, 68 (1978).
9. R. Asami, M. Takaki, Y. Harima, and H. Tsuzuki, *Polym. J.*, **13**, 141 (1981).
10. L. Garrido, J. Guzman, and E. Riande, *Macromolecules*, **14**, 1132 (1981).