

Cationic Polymerization of 2,3-Dihydrofuran. Study on the Relationship between Glass Transition Temperature and Tacticity of the Polymer

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ABSTRACT: The cationic polymerization behavior of 2,3-dihydrofuran (DHF) was investigated. Polymerization of DHF was carried out in the presence of boron trifluoride (BF_3) or ethylaluminum dichloride (EADC). The glass transition temperature (T_g) of the polymer depended upon the polymerization conditions. The T_g of the polymer obtained in the polymerization with BF_3 at -78°C was 150°C . On the other hand, the T_g of the polymer obtained in the polymerization above -60°C was ca. 130°C . In the polymerization with EADC, addition of ethyl acetate increased the molecular weight of the polymer compared to that of polymerization in toluene only. In the ^{13}C -NMR spectra of the polymer, splits of signals of main chain carbon atoms which corresponded to erythro and threo isomers were observed. A linear relationship between the ratio of isomers and T_g was confirmed. The all-trans conformer of the threo-diisotactic isomer was concluded to be the most stable one from MM2' calculation. ^{13}C -NMR and molecular mechanics studies suggested that the difference in T_g of the polymers was derived from the difference in tacticity of the polymers.

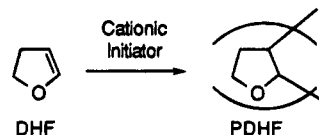
Introduction

Cationic polymerizations of electron-rich vinyl monomers such as vinyl ether and isobutene are important since these monomers afford polymers with high molecular weight only by cationic polymerization. Recently, polymers having narrow molecular weight distributions have been to be prepared by the living cationic polymerization technique developed by Higashimura and Sawamoto et al.¹ 2,3-Dihydrofuran (DHF), a cyclic vinyl ether, and its derivatives are reported to undergo polymerization with cationic initiators such as boron trifluoride (BF_3),² diethylaluminum chloride,³ iodine,⁴ and acetyl perchlorate⁴ to afford polymers having a poly(2,3-tetrahydrofurandiyl) (PDHF) structure (Scheme 1). A softening temperature (118°C) of PDHF is reported;² however, detailed polymerization behavior such as tacticity of PDHF is hardly known. In this paper, the detailed cationic polymerization behavior of DHF and the relationship between the glass transition temperature and tacticity of PDHF are presented.

Experimental Section

Measurements. ^1H - and ^{13}C -NMR spectra were recorded at 27°C on a JEOL JNM-GX-500 spectrometer with tetramethylsilane (TMS) as an internal standard in deuteriochloroform. FT-IR spectra were obtained with a Digilab FTS-20C/T at 25°C . Conversion of DHF was determined by gas chromatography (GC) on a Shimadzu GC-7AG with a data processor, equipped with a packed column (liquid phase; Thermo-1000 5%, solid support; Chromosorb W [AW-DMCS]) with nitrogen as an eluent, FID detector. The water content of a solvent was measured with a Mitsubishi Chemical Industries water content analyzer CA-05. Molecular weight and its distribution (\bar{M}_w/\bar{M}_n) were determined by gel permeation chromatography (GPC) on a Shimadzu LC-6A system with a data processor, equipped with three polystyrene gel columns

Scheme 1



(Shim-pack, HSG-20H, HSG-40H, and HSG-60S), with tetrahydrofuran (THF) as an eluent, flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Thermal analyses were performed on a Mettler TA3000 system. The glass transition temperature (T_g) by differential scanning calorimeter (DSC) was taken as the inflection point on the trace.

Materials. DHF, toluene, dichloromethane, *n*-hexane, and ethyl acetate were dried and distilled over calcium hydride just before use. Initiators [BF_3 (Hashimoto Chemical Industries) and ethylaluminum dichloride (EADC, 1 M solution in *n*-hexane, Wako Chemical Industries)] were used as received. BF_3 solutions were prepared by bubbling BF_3 into solvents. The concentration of a BF_3 solution was determined by titration of the mixture of the BF_3 solution and water (volume ratio, 1:5) using standard hydrochloric acid with phenolphthalein as an indicator.

Polymerizations of DHF. General Procedure. To a 14.5 mM solution of BF_3 in toluene (10 mL) was added DHF (2.0 g, 29 mmol) dropwise at -78°C . After that, the reaction mixture was stirred for 48 h. Polymerization was stopped by the addition of 1 M ammonia solution in methanol (0.5 mL, 0.5 mmol) at -78°C . The resulting mixture was diluted with toluene (10 mL) and precipitated into methanol (400 mL) to isolate the polymer. Conversion: 30%. Yield: 0.50 g (25%). \bar{M}_n 44 600, \bar{M}_w/\bar{M}_n 2.03. ^1H NMR (CDCl_3): δ 1.4–2.9 (broad s, 3 H), 3.5–4.5 (broad s, 3 H) ppm. ^{13}C NMR (CDCl_3): δ 25–32, 39–50, 65–69, 77–86 ppm. IR (film cast from THF): 2950, 2860, 1455, 1200, 1062, 920, 690 cm^{-1} . Anal. Calcd for $\text{C}_4\text{H}_6\text{O}$: C, 68.55; H, 8.63. Found: C, 68.75; H, 8.88.

Molecular Mechanics Calculations. All calculations were done on a Hitachi HITAC M-640 with use of the MM2' program, 1982 version.⁵ Starting geometries were obtained by a Hitachi MODEL MATE system. In the VDW calculations, the hydrogen atoms are relocated so that the attached hydrogen distance is reduced by 0.915. Energy is minimized within 0.005 kcal.

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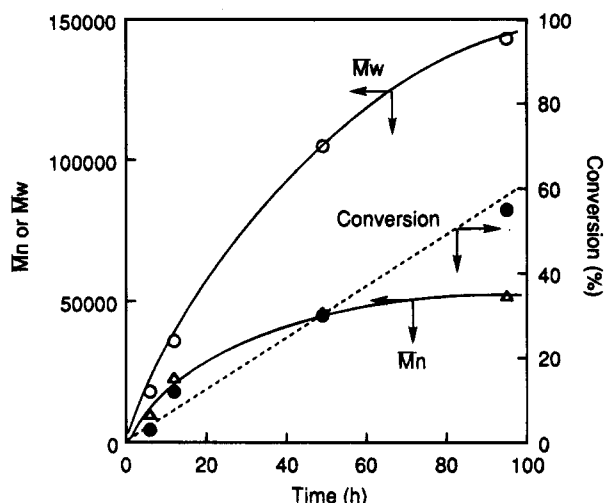


Figure 1. Time-conversion and time-molecular weight curves in the polymerization of DHF with BF_3 as an initiator. Conditions: DHF, 29 mmol; toluene, 10 mL; -78°C ; $[\text{BF}_3]/[\text{DHF}]_0 = 0.5$ mol %.

Results and Discussions

1. Cationic Polymerization of DHF. Time-conversion and time-molecular weight curves in the polymerization of DHF at -78°C with a typical cationic initiator, BF_3 , are shown in Figure 1. The rate of the polymerization was relatively slow, and living-like polymerization character was observed. In the polymerization at 25°C with EADC (1.3 mol % vs DHF),⁶ DHF was converted to 100% within 1 min. The heat of polymerization was large in this case and the scale of the polymerization was small, strict control of polymerization temperature was difficult. Therefore, the temperature of the polymerization mixture increased to ca. 40°C .

A white fibrous polymer was obtained in the polymerization with BF_3 at -78°C after isolation by reprecipitation into methanol. On the other hand, a pale yellow sticky polymer was obtained in the polymerization with EADC at 25°C . The structure of the polymer obtained was poly(2,3-tetrahydrofurandiyl) (PDHF) which was formed by vinyl polymerization. A ring-opened unit was not observed at all from ^1H - and ^{13}C -NMR spectral analyses. Results of cationic polymerization of DHF under several conditions are summarized in Table 1.

In cationic polymerization with Lewis acid initiators such as BF_3 and EADC, the necessity of a cocatalyst (water) is reported.⁷ Excess water above the amount of the initiator must be avoided because it inactivates the initiator. In this study, water content (measured

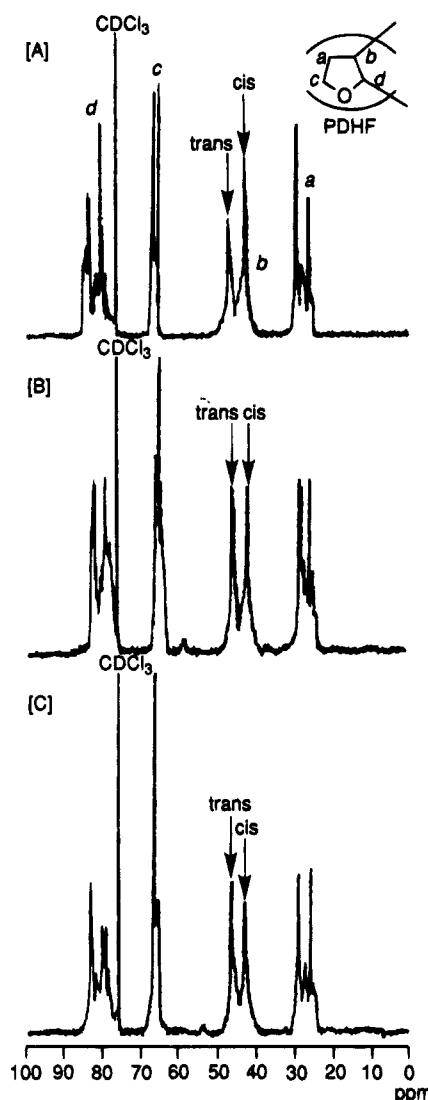


Figure 2. ^{13}C NMR spectra (CDCl_3 , 125 MHz) of PDHF. (A) obtained in the polymerization with BF_3 at -78°C , T_g 151°C ; (B) obtained in the polymerization with BF_3 at -60°C , T_g 127°C ; (C) obtained in the polymerization with EADC at 25°C , T_g 116°C .

on a water content analyzer according to the Karl Fischer method) in a solvent was strictly controlled and kept under 50 ppm. In the polymerization with BF_3 as an initiator in toluene, a polymer having a high molecular weight (\bar{M}_n ; 44 600) and T_g (150°C) was obtained in 30% conversion at -78°C (run 1 in Table 1). In the polymerization with BF_3 in *n*-hexane, conversion and molecular weight decreased drastically (run 4 in Table 1). Insolubility of the polymer in *n*-hexane may cause

Table 1. Cationic Polymerization of DHF^a

run	init ^b	solv	temp ($^\circ\text{C}$)	time (h)	conv ^c (%)	yield ^d (%)	\bar{M}_n^e	\bar{M}_w/\bar{M}_n^e	T_g^f ($^\circ\text{C}$)
1	BF_3	toluene	-78	48	30	25	44600	2.03	150
2	BF_3	toluene	-60	48	97	90	38300	2.31	127
3	BF_3	toluene	-20	2	100	94	g	g	129
4	BF_3	<i>n</i> -hexane	-78	48	2	2	8600	2.05	
5	BF_3	dichloromethane	-78	48	73	70	52900	2.07	131
6	EADC	toluene	-78	48	36	33	44100	1.80	134
7	EADC	toluene	25	2	100	93	13700	3.13	125
8	EADC	toluene/ethyl acetate = 10/1	25	2	100	96	27000	2.27	124
9	EADC	<i>n</i> -hexane/ethyl acetate = 10/1	25	2	100	94	10000	6.25	
10	EADC	<i>n</i> -hexane	25	2	100	95	16800	4.63	

^a Conditions: DHF, 2 g (29 mmol); solvent 10 mL. ^b BF_3 : boron trifluoride, 0.5 mol % vs DHF. EADC: ethylaluminum dichloride 1.3 mol % vs DHF. ^c Estimated by GC. ^d Methanol-insoluble part. ^e Estimated by GPC (based on polystyrene standards). ^f Estimated by DSC.

^g Cross-linked polymer was obtained.

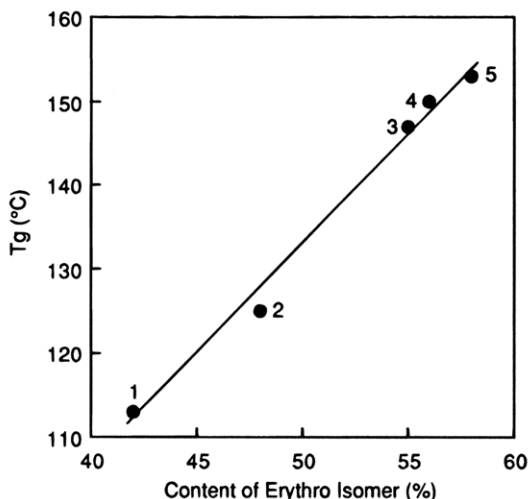


Figure 3. Relationship between the ratio of isomers determined by ^{13}C NMR spectra and T_g of PDHF: (1) obtained in the polymerization of 290 mmol of DHF with EADC at 25 °C; (2) obtained in the polymerization of 29 mmol of DHF with EADC at 25 °C; (3) obtained in the polymerization of 290 mmol of DHF with BF_3 at -78 °C; (4) Obtained in the polymerization of 29 mmol of DHF with BF_3 at -78 °C; (5) obtained in the polymerization of 10 mmol of DHF with BF_3 at -78 °C.

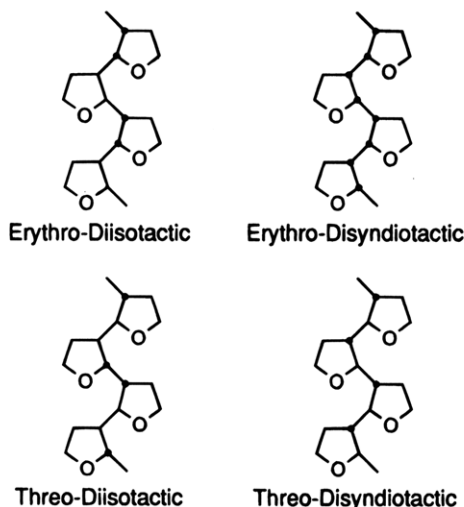


Figure 4. Possible four regular stereoisomers of PDHF.

the difference. The T_g of the polymer decreased to 127 °C as polymerization temperature was raised to -60 °C (run 2 in Table 1), in which conversion approached 97%. A polymer insoluble in common organic solvents was obtained with quantitative conversion in the polymerization at -20 °C (run 3 in Table 1). Cross-linking reactions such as ring-opening in addition to vinyl polymerization, most likely occur in this case. The polymer obtained in the polymerization in dichloromethane showed a higher molecular weight (\bar{M}_n ; 52 900) but lower T_g (131 °C) (run 5 in Table 1) than that obtained in the polymerization in toluene (run 1 in Table 1). In the polymerization with EADC as an initiator, cross-linked polymer was not obtained even at 25 °C (runs 7–10 in Table 1). Polymerizations with EADC at 25 °C were completed in a very short period. The molecular weight distribution of the polymer obtained in the polymerization in *n*-hexane was larger than that obtained in the polymerization in toluene (runs 7 and 9 in Table 1). Addition of ethyl acetate increased the molecular weight and decreased the molecular weight distribution of the polymer obtained (runs 7, 8 and 9, 10 in Table 1). The carbonyl

Table 2. Most Stable Conformers of the Isomers of PDHF and Their Steric Energy^a

	erythro-diisotactic	erythro-disyndiotactic	threo-diisotactic	threo-disyndiotactic
most stable conformer ^b	AAA	+A+	AAA	+ - +
steric energy (kcal/mol)	49.69	52.41	44.09	46.17

^a Calculated by the MM2' method for tetramer models. ^b A, anti; +, gauche (+); -, gauche (-).

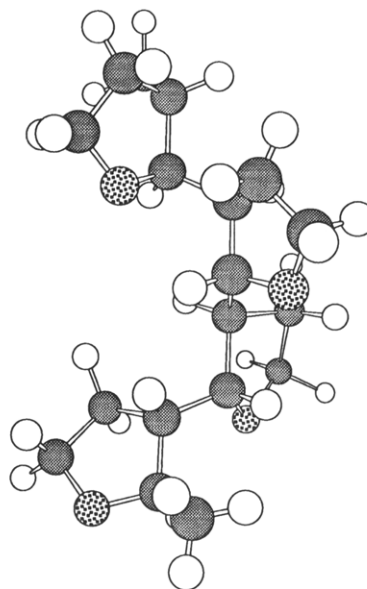
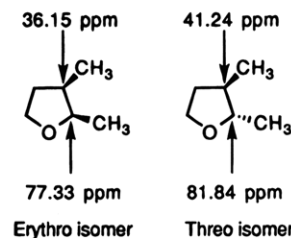


Figure 5. Most stable conformer of the threo-diisotactic isomer of PDHF determined by the MM2' calculation.

oxygen atom of ethyl acetate should stabilize the cationic propagation end.^{6b} In conclusion, polymerization with BF_3 at -78 °C is the most superior way to obtain PDHF having both a high molecular weight and high T_g .

2. Higher Order Structure. As described above, the T_g of PDHF varies with the polymerization condition. Higher order structure of PDHF must be related with this phenomenon. First, ^{13}C NMR analysis of PDHF was carried out. Four signals were observed in the spectra, and the signals assigned to main chain carbon atoms (b and d) were split by 5 ppm (Figure 2).⁸ This split should be derived from erythro and threo configurations of the main chain because of the difference of chemical shifts of erythro- and threo-2,3-dimethyltetrahydrofuran, as illustrated below.⁹ The signals at higher and lower fields are assigned to erythro and threo carbons, respectively. A linear relationship between the ratio of isomers and T_g was observed (Figure 3).¹⁰



Secondly, the conformation of PDHF was examined by a molecular mechanics study. Erythro-diisotactic, erythro-disyndiotactic, threo-diisotactic, and threo-disyndiotactic are possible as regular stereo isomers of

PDHF (Figure 4). MM2' calculations for the models of each isomer consisting of four repeating units were carried out. Steric energies of the most stable conformers of each isomer were summarized in Table 2.

A threo-diisotactic isomer having the all-trans conformation was the most stable. This conformer forms a spiral structure and the ether oxygen is directed outside of the main chain (Figure 5).¹¹ The threo-diisotactic isomer has the threo configuration at the main chain. This isomer corresponding to the polymer having a low T_g by ¹³C-NMR analysis. Since the polymerization at high temperature has afforded a polymer having a low T_g , the polymerization that affords the threo isomer should be under thermodynamic control and that which affords the erythro isomer should be under kinetic control.

Conclusion

In this paper, the cationic polymerization behavior of 2,3-dihydrofuran (DHF) was investigated. The polymer having the poly(2,3-tetrahydrofurandiyl) structure showed different T_g 's according to the polymerization conditions. Polymerization at lower temperatures afforded a polymer having a higher T_g , and vice versa. From the ¹³C-NMR and molecular mechanics studies, it was concluded that the difference of T_g of the polymers was derived from the difference in tacticity of the polymers. Namely, polymerization at low temperatures predominantly afforded a high content of erythro isomer having a high T_g .

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Supporting Information Available: Starting and final atomic coordinates and bonded atom tables of the threo-diisotactic isomer of PDHF (2 pages). Ordering information is given on any current masthead page.

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