Preparation of Narrow-Molecular-Weight-Distribution Poly(tetrahydrofuran)

Teruo FUJIMOTO, Masaru KAWAHASHI, Mitsuru NAGASAWA,
and Akira TAKAHASHI*

Department of Synthetic Chemistry, Nagoya University, Nagoya 464, Japan.

**Chemistry Department of Industry and Resources, Mie University,
Tsu, Mie 514, Japan.*

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ABSTRACT: The preparation method for the monodisperse crystallizable polymer, poly(tetrahydrofuran), was studied over a wide range of molecular weights. Bulk polymerization of tetrahydrofuran (THF) was carried out by introducing THF monomer into a completely reacted trifluoroboron—THF—ethylene oxide catalyst—promoter system, with vigorous stirring. This initiation technique had no induction period. Both molecular weights and conversion increased linearly with reaction time. The molecular weight distribution evaluated by the sedimentation method as well as light scattering and osmometry was very sharp and $\bar{M}_w/\bar{M}_n$ was less than 1.01 even at the $\bar{M}_w=10^6$. When the polymerization is stopped at a low conversion (8%), which is far from the equilibrium, the in-chain transfer reaction is negligible.

KEY WORDS Poly(tetrahydrofuran) / Narrow Molecular Weight
Distribution / Trifluoroboron—THF—Ethylene Oxide / Catalyst—
Promoter / Impurity / Chain Transfer /

Much progress has been made in the study of the physical properties of amorphous polymers since the preparation of monodisperse polystyrene by Szwarc.¹ It seems unnecessary to stress the importance of monodisperse crystallizable polymers in the study of polymer physics. A few monodisperse crystallizable polymers [poly(tetrahydrofuran), poly(ethylene oxide) have] been prepared.

The purpose of this work is to study the preparation method for the monodisperse crystallizable polymer, poly(tetrahydrofuran) (PTHF), over a wide range of molecular weights. It was pointed out^{2,3} that tetrahydrofuran (THF) can be polymerized on a living mechanism, by certain ring opening cationic initiators, and several papers^{4–10} have been published on the preparation of PTHF of narrow molecular weight distributions. However, these molecular weight distributions are not narrow enough and the molecular weight ranges covered are not wide enough. It is essential in the study of physical properties to have samples not only with sharp molecular weight distributions but also a wide molecular weight range.

There are various cationic initiators presented in previous works: trifluoroboron (BF₃)—ethylene

oxide (EO) catalyst,^{4,5} triethyloxonium hexachloroantimonate,⁶ trifluoromethanesulfonic anhydride,⁷ and *p*-chlorophenyldiazonium hexafluorophosphate.⁸ If triethyloxonium hexachloroantimonate, trifluoromethanesulfonic anhydride and *p*-chlorophenyldiazonium hexafluorophosphate are selected as initiators, the active chain ends may cause chain transfer reactions and, moreover, the products produced when they react with impurities (*e.g.* SbCl₅, CF₃SO₃H, PF₅) may be able to undergo slow initiation by dimerization.² Those unfavorable reactions may broaden the molecular weight distributions of the products and, in practice, the polydispersity ratio ($\bar{M}_w/\bar{M}_n$) reported in literature is 1.04—1.08. It was reported by Croucher and Wetton⁸ that the PF₅[–] gegenion of the initiator should be kept above the ceiling temperature. This is probably because of the production of PF₅.¹¹ Such unfavorable side reactions do not occur in the polymerization of THF with triethyloxonium tetrafluoroborate and BF₃—THF catalyst. However, the ratio $\bar{M}_w/\bar{M}_n$ of PTHF was found to be almost 2 by Makletsova, *et al.*¹² Taking this literature into account, we selected a catalyst—promoter system; that is, the BF₃—THF complex as a catalyst and

ethylene oxide as a promoter.

With this initiator, Johnston⁴ obtained a very low molecular weight PTHF, the molecular weight distribution being somewhat broader than the Poisson distribution. Ofstead⁵ obtained also PTHF with $\bar{M}_w/\bar{M}_n=1.04$ for low molecular weight samples; however, the high molecular weight samples had rather broad molecular weight distributions. To obtain very high molecular weight samples with narrow molecular weight distribution, it is necessary to use very low catalyst concentration since the molecular weights are inversely proportional to catalyst concentration. Moreover the reaction probability between catalyst and promoter in the initiation stage should be very low when using the mixing procedure of Johnston and also of Ofstead. Therefore, to avoid a possible delayed initiation stage compared with propagation, which may lead to broadening of molecular weight distribution, we used a different order of mixing of catalyst—promoter and monomer to that employed by Johnston⁴ and Ofstead.⁵ In this catalyst system, it is necessary to add a promoter such as EO, propylene oxide (PO) and as well as epichlorohydrine (ECH). Saegusa, *et al.*,¹⁰ reported that EO and ECH are more effective than PO as promoter. However, Booth, *et al.*,^{13,14} reported that the melting temperatures of polyether such as poly(ethylene oxide) are much affected by the character and structure of end group, especially by chlorine atom. Since crystallization and melting of low molecular weight PTHF with OH end group have been reported by several authors,¹⁵⁻¹⁷ we preferred here to use EO as a promoter in the study of the molecular weight dependence of the crystallization of PTHF.

PREPARATION

Purification of THF and EO

The apparatus and technique for the purification of THF and EO were similar to those described previously.¹⁸ The vacuum line was pumped to 10^{-6} mmHg pressure. THF (Katayama Chemical Co.) was fractionally distilled by a conventional procedure and then refluxed over sodium metal for several hours. This procedure was repeated twice and THF was distilled into a flask containing a few pieces of sodium and anthracene. The liquid was repeatedly degased at -78°C and re-

fluxed until a permanent blue color remained. EO gas was collected as liquid in a flask by cooling it with dry-ice—acetone. The EO liquid was dried with CaH_2 for hrs. *in vacuo*, and then fractionally distilled twice *in vacuo*.

Preparation of the Initiator, BF_3 —THF Complex

BF_3 —THF complex was prepared by a reaction of BF_3 gas with liquid THF. A flask containing purified THF was filled with dry N_2 gas, and then BF_3 gas flowed into the liquid THF through a capillary. After reacting BF_3 with THF for about 1 h the inlet tube for the BF_3 gas was sealed off. The complex formed was solidified by cooling it to -78°C and the whole apparatus was evacuated. The complex was fractionally distilled twice *in vacuo*. The fraction in the range of 58 – 60°C under 10^{-6} mmHg was collected.

Polymerization

The bulk polymerization of THF was carried out in the apparatus shown in Figure 1, in which F is the reaction vessel, A, B, C, and D flasks serving as sampling flasks for the reaction mixture. Flask T_1 contains monomer THF, ampules T_2 , I and P contain THF used for washing the apparatus, BF_3 —THF complex and the promoter EO; respectively, and ampule E was used to collect THF after washing the apparatus. The polymerization was performed at 10^{-6} mmHg in the following manner. (1) The breakable seal of the ampule I was broken and the BF_3 —THF complex was introduced into flask F. (2) The breakable seal of T_2 was opened and ampule I was washed with THF. This THF

Figure 1. Apparatus for polymerization: symbols are shown in the text.

was put into flask E and sealed off. (3) The breakable seal of the promoter ampule P, made by a calibrated capillary on inner diameter $\phi = 0.2$ mm, was opened and EO was transferred into flask F with vigorous stirring to react with BF_3 —THF complex. To ensure the complete transfer of EO into the reaction flask F, flask F was cooled by dry-ice—acetone and the apparatus was warmed for 30 min. By doing so, the catalyst—promoter reaction between EO and BF_3 —THF complex was completed. The completion of the reaction between EO and BF_3 —THF complex was confirmed by observing that no EO condensed on the ampule P wall when ampule P was cooled by dry ice—acetone. Then, the breakable seal of T_2 was broken, keeping the temperature of flask F at 0°C and stirring the flask F with a magnetic stirrer. The bulk polymerization of THF started immediately. At appropriate times, the reaction mixture was transferred into flasks A, B, C, and D which were sealed off at a scheduled time. The PTHF formed at different reaction times was precipitated as solid cakes, by pouring the reaction mixtures into dilute NaOH aqueous solutions. The precipitated polymers were purified by repeating the dissolution and precipitation with THF and H_2O . After vacuum drying, the polymer was again dissolved in benzene and freeze-dried.

MEASUREMENTS

Molecular Weight Determination

The weight-average molecular weights were determined from light scattering measurements, using modified Shimadzu light scattering photometer described previously.¹⁹ The calibration of the instrument was carried out by using both

benzene and NBS standard polystyrenes. Ethyl acetate was employed as the solvent, and measurements were carried out at 30°C with 436 nm by using a differential refractometer of the Debye type. All solutions were cleaned by filtration through membrane filters Dularon-NRWP 04700 25 *ca.* NR. A typical Zimm plot obtained is shown in Figure 2.

The number-average molecular weights were determined by using a Mechrolab high speed membrane osmometer, Model 502, fitted with a membrane 0—8. Toluene was used as solvent and the measurements were carried out at 25°C . Intrinsic viscosities of the samples in benzene or in toluene were measured with a modified Ubbelohde viscometer. The viscosity-average molecular weights were calculated according to the following equations.

$$[\eta] = 1.31 \times 10^{-3} \bar{M}_n^{0.60} \quad (\text{Benzene, } 30^\circ\text{C}) \quad (1)^{20}$$

$$[\eta] = 2.36 \times 10^{-4} \bar{M}_n^{0.77} \quad (\text{Toluene, } 30^\circ\text{C}) \quad (2)^5$$

The values of $\bar{M}_v$ calculated from both equations agreed each other and also agreed with the values of $\bar{M}_n$ determined directly.

Molecular Weight Distribution Determination from Sedimentation Velocity

The molecular weight distributions of selected samples were measured by the sedimentation velocity method. A Spinco Model E ultracentrifuge was used, and the sedimentation experiments were performed at 59760 rpm. using a mixed θ solvent, that is, a mixture of hexane (77.3 wt %) and ethylacetate (22.7 wt %) at 30.4°C .²⁰

Care was taken that the sample solution should not be cooled below the θ temperature before being placed in a centrifuge cell. Kurata, Utiyama, and Kamada²⁰ reported the concentration dependence of the sedimentation velocity of PTHF in the mixed solvent, at a slightly higher operation temperature, and observed a small concentration dependence. However, on employing such dilute solutions as 0.1 g/100 ml, we found that sedimentation velocity was independent of the polymer concentration. Thus, the molecular weight distribution was calculated from sedimentation patterns at one concentration between 0.1 and 0.15 g/100 ml. A correction for diffusion was obtained by extrapolating the results obtained at different times to an infinite time; but no correction was made for the

Figure 2. An example of the Zimm plot of sample T-3-5 in ethyl acetate solution at 30°C : C_p , polymer concentration in g/dl; R_θ , the Rayleigh scattering ratio at the angle θ ; K , the optional constant.

pressure effect. The actual calculation procedure of the molecular weight distribution from sedimentation patterns followed the method of Homma, Kawahara, Fujita and Ueda.²¹

RESULT AND DISCUSSION

The viscosity average molecular weights of the polymers at different polymerization times in an experiment are listed in Table I. The conversion vs. reaction time is also plotted in Figure 3. It is

Table I. Bulk polymerization of tetrahydrofuran (THF) of T-3 series

Sample No.	Polymerization time, min	Conversion, %	$\bar{M}_v \times 10^{-4}$
T-3-1	65	2.05	3.9
2	120	3.40	7.7
3	178	4.42	9.3
4	248	5.41	10.5
5	363	8.68	18.1

^a THF, 12.3 mol/l; BF₃—THF, 0.051 mol/l; EO, 0.0016 mol/l.

Figure 3. Plot of conversion vs. reaction time for T-3 series in Table I.

evident from the figure that no induction period is observed in the present experiments. Ofstead⁵ observed an induction period of several minutes, though he used the similar catalyst-promoter system. This difference may result from the difference in the manner of addition of the catalyst, the promoter, and the monomer into the reaction flask F. In the experiment of Ofstead, the BF₃—THF complex was injected over a period of 10 s into the THF monomer which already contained EO, whereas we first completely reacted the BF₃—THF complex with EO, and then intro-

Figure 4. Plot of molecular weight vs. reaction time for T-3 series in Table I.

Figure 5. Plot of molecular weight vs. reaction time for T-3 series in Table I.

duced THF monomer with vigorous stirring.

Figure 4 shows the relationship between the molecular weight and the reaction time in the experiment of Table I. The plot is linear and passes through the origin. Thus, the relationship between the conversion and molecular weight is also linear, as is shown in Figure 5, showing the living polymerization of THF. Although we could not obtain enough conversion data in other experiments, the molecular weight increased almost linearly with time in the experiments, as shown in Table II.

If there is no induction period and the polymerization proceeds under an equilibrium condition, the polymerization rate is expressed as²²

$$-d[M]/dt = k_p[M^*]\{[M] - [M]_e\} \quad (3)$$

where $[M^*]$, $[M]$ and $[M]_e$ are the active species, instantaneous and equilibrium monomer concentrations, respectively. The concentration of active species can be calculated from the amounts of polymer obtained and their molecular weights. At a reaction temperature of 0°C, the equilibrium monomer concentration has already been estimated from the data of Smith and Dreyfuss, *et al.*,^{2,8} to be 1.70 mol/l. The values of $\ln \{[M]_0 - [M]_e\}$

Table II. Bulk polymerization of THF of other series

Sample No.	Monomer, mol/l	BF ₃ —THF × 10 ² , mol/l	EO × 10 ³ , mol/l	Polymerization time, min	$\bar{M}_n \times 10^{-4}$
T-1-1	} 12.3	} 6.8	} 6.5	35	1.3
2				65	2.3
3				120	4.2
T-2-1	} 12.3	} 3.4	} 0.95	375	27.8
2				721	49.5
3				1115	87.0
T-4-1	} 12.3	} 8.5	} 26	27	1.4
2				40	6.5
T-5-1	} 12.3	} 2.1	} 0.23	1333	51.5
2				2723	80.0
3				4288	100
T-6-1	} 12.3	} 2.1	} 0.12	2980	140
2				7125	170
3				11425	180

Figure 6. Plot of $\log\{([M]_0 - [M]_e)/([M] - [M]_e)\}$ vs. reaction time. $[M]_0$, $[M]$, and $[M]_e$ are initial, instantaneous, and equilibrium concentration of the monomer.

$[M] - [M]_e$ are calculated from the data in Table I with this value of $[M]_e$ and plotted against reaction time, as shown in Figure 6. The propagation rate constant, k_p , can be determined as 0.276 l/mol min. from the slope. This value is in good agreement with the value, 4.83×10^{-3} l/mol s, reported by Tobolsky, *et al.*,²² but is twice as high as that reported by Croucher, *et al.*⁸ In the polymer prepared from the THF by using the BF₃—THF complex and EO, it must be considered that there is at least one EO unit in each polymer chain. The number of EO units can be calculated from the amount of polymer obtained, EO charged, and their molecular weights. It was found that there are three to five EO units for each polymer chain

in sample T-3 or T-2 series.

The weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights determined by light scattering and osmotic pressure measurements are listed in Table III, together with the ratio $\bar{M}_w/\bar{M}_n$. The molecular weight distributions of the polymers calculated from sedimentation experiments are shown in Figure 7, and the values of $\bar{M}_w/\bar{M}_n$

Table III. Molecular weight and molecular weight distribution

Sample No.	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w/\bar{M}_n^a$, sed
T-1-3	4.0	4.2	1.0 ₅	1.07
T-2-3		83.3		1.00 ₁
T-3-5	16.7	17.6	1.0 ₅	1.00 ₉
T-5-1		51.3		1.00 ₅

^a From sedimentation experiments.

Figure 7. Molecular weight distribution: A, T-1-3; B, T-3-5; C, T-2-3.

Figure 8. Sedimentation velocity of sample T-3-5 at various concentrations in ethyl acetate and hexane mixed solvent at 30.4°C.

calculated from the distribution curves are also listed in Table III. The ratio $\bar{M}_w/\bar{M}_n$ which is usually used to express the degree of molecular weight distribution is close to unity. The molecular weight distribution of PTHF obtained by this method may thus be concluded to compare sharply with those so far published. To show the reliability of such a sharp molecular weight distribution, the sedimentation constants of molecules at various concentration points in a sedimentation pattern are plotted against inverse time in Figure 8 in relation to the sedimentation constant at the half concentration point. The sample is T-3-5 in Table I. S and $S_{0.5}$ are the sedimentation constants of the molecules which are at the positions of concentration C and $0.5 C_0$ respectively, (where C_0 denotes the initial concentration). All straight lines at different C/C_0 converge in the vicinity of unity at $1/t=0$, in agreement with previous results for poly α -methylstyrene obtained by anionic polymerization.¹⁸

In the bulk polymerization of THF, slow initiation reactions, the equilibrium effect between the active chain end and monomer and also the possible chain transfer reactions may be the factors causing a broadening of the molecular weight distribution of PTHF.^{2,8} Since the induction period is not observed in this experiments and the number of active species should be proportional to the amount of EO and BF_3 —THF complex, the velocity of initiation with the present catalyst—promoter system may be much faster than that of propagation. The

molecular weight distribution cannot be narrow if polymerization—depolymerization equilibrium is attained; but in these experiments, polymerization was stopped considerably before equilibrium was attained, at a conversion below 8%. The second effect may be negligible.²⁴ Although the level of impurities in our system is very low, it may be true that there are possible chain transfer reactions in the present polymerization system; that is, the reaction of in-chain oxygens of the polymer with growing species and the reaction of the growing chain-ends with counter ions. In particular, the latter chain transfer reaction may occur easily when the counter ion is BF_4^- rather than SbF_6^- and PF_6^- . However, it may be concluded from the present experimental results that these chain transfer reactions are negligible in the present polymerization system.

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