Photoinduced Living Cationic Polymerization of Tetrahydrofuran(IV): Syringe Method

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ABSTRACT: The living nature of cationic poly(tetrahydrofuran), which is generated by the addition of the photolytic products of diphenyliodonium hexafluorophosphate (initiator) via syringe, was investigated in connection with the direct polymerization method in which polymerization of tetrahydrofuran is carried out in the presence of the initiator. Although the living nature of the polymerization (i.e., the linear relationship between the percentage of conversion and the molecular weight of the resulting polymer) is observed in the syringe method because of the absence of chain transfer or termination, unexceptionally, a lower rate of polymerization and higher molecular weights of the resulting polymers were observed in the syringe method when compared with those of the corresponding direct polymerization method. This leads us to the conclusion that the living nature is ascribed to the stabilization of the propagating cationic species due to ion pair formation with the less-nucleophilic complex metal halide anion (PF_6^-), and the decreased rate of polymerization and higher molecular weight in the syringe method is attributed to the partial loss of the activity of the cationic species because of the nucleophilic attack of basic impurities, such as water, introduced to the system in the syringe manipulation. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2082–2087, 2002

Key words: photoinduction; living cationic polymerization; tetrahydrofuran; syringe method

INTRODUCTION

Living polymers have been the subject of extensive studies because living polymer systems enable us to synthesize monodispersed[1] and terminally functional polymers,[2,3] block copolymers by sequential polymerization,[4,5] block copolymers by terminal functionalization followed by polymerization,[6] block copolymers by an ion-coupling reaction, and graft copolymers.[7]

In our previous investigations on photoinduced cationic polymerization of tetrahydrofuran (THF) in the presence of diphenyliodonium hexafluorophosphate (initiator),[8–10] we reported that a cationic polymerization of THF is initiated by the addition of a proton, a photolytic product of the initiator.[11–17] The living nature of the system is from the stabilization of the propagating cationic species, a five-membered cyclic oxonium ion, by ion pair formation with a complex metal halide anion supplied by the initiator.[9] However, the living nature does not appear unless the system is prepared under strictly dried conditions because the activity of the propagating cationic species is lost by the nucleophilic attack of water.

In this article we report the results of living cationic polymerization of THF, which is initiated by the addition of the photolytic products of the initiator using the syringe technique.

EXPERIMENTAL

Materials

The THF (Tongyang Chemicals) was stored and dried for several weeks on CaH_2 (Sigma) after purification by conventional fractionation on $LiAlH_4$ and repurified by distillation under reduced pressure just prior to use. Reagent grade diphenyliodonium hexafluorophosphate (Tokyo Kasei), pyridine (Tongyang Chemicals), benzoyl chloride (Aldrich), sodium hydrogen carbonate (Tongyang Chemicals), and chloroform-*d* (Aldrich) were used without further purification.

Photoinduced Polymerization

Polymerization experiments were carried out in two different ways: direct polymerization and the syringe method. In the syringe method the polymerization was initiated by the addition of the photolytic products of the initiator. A syringe was used for introduction of the photolytic product to the THF through a rubber septum. In the direct polymerization method the polymerization was initiated by UV irradiation of the THF in the presence of the initiator.

Direct Polymerization Method

Strictly dried THF on CaH_2 was introduced to a Pyrex ampoule where the dried initiator was placed and then the ampoule was sealed off after repeated degasing. A 500-W high-pressure mercury lamp (Ushio UI-501-C) was used as a light source for the photoinduced polymerization at 0°C for 30 min, which was followed by a dark reaction at 0 or 30°C. The polymers were precipitated in excess distilled water and washed successively with water and THF. The percentage of conversion was determined by gravimetry after drying under reduced pressure at ambient temperature for 24 h.

Syringe Method

Two ampoules with two inlets, one equipped with a ground joint and the other equipped with a rubber septum, were used in the syringe method. One ampoule is filled with THF, and the other is
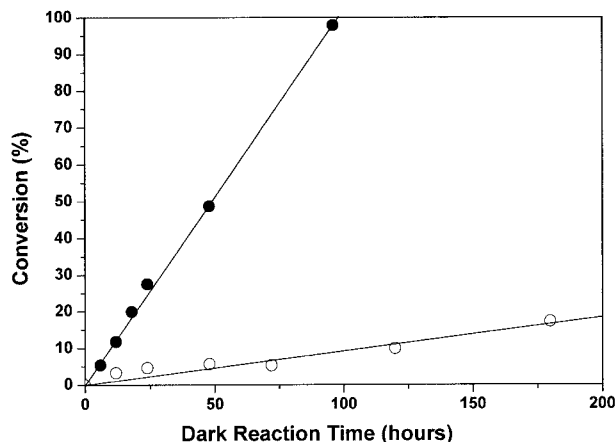

Figure 1 Time–conversion curves of photoinduced cationic polymerization of THF by the (●) direct polymerization method and (○) the syringe method in the presence of $0.05M$ initiator and carried out in the dark at 0°C. Photoirradiations for the two methods were carried out under the same conditions at 0°C for 30 min.

filled with a THF solution of the initiator for the UV irradiation. The initiator was thoroughly dried *in vacuo* at 100°C before filling it with THF. After sealing off, the ampoule of the THF solution of the initiator was irradiated under the same condition as that of the direct photoinduced polymerization, and then the photolytic products were syringed to the ampoule filled with THF. Prompt syringe manipulation was an essential technique to minimize the exposure of the photolytic products to the air. The syringed ampoule was placed in the dark at 0 or 30°C for further reaction. Similar procedures were used for the polymer treatment after the completion of the polymerization with the direct polymerization method.

Analysis

The number-average molecular weight (M_n) and its distribution of the resulting polymers were determined by gel permeation chromatography (8430 RI, Spectra Physics) using THF as a solvent with a flow rate of 1 mL/min and 10^3, 10^4, and 10^5 Å columns used in series. The number of functionalities of the polymer was determined by a ^{1}H-NMR spectrometer (Jeol PMX 60SI) using $CDCl_3$ as a solvent.

RESULTS AND DISCUSSION

Figure 1 shows time–conversion curves of THF polymerization carried out at 0°C. The results of

the direct polymerization method are also shown for the sake of comparison. It shows that the percentage of conversion increases linearly with the reaction time in both cases, which means that THF is initiated by the photolytic products of the initiator, presumably hexafluorophosphoric acid, as reported by Crivello and Lam[12–16]; however, the rate of polymerization in the syringe method is lower than that of the corresponding direct polymerization method, as reported in our previous article.[8]

Photolysis of the initiator[12] proceeds as follows:

$$\text{(diphenyliodonium PF}_6^-\text{)} \xrightarrow{h\nu} \text{Ph–I} + \text{Ph–Ph} + \text{Ph} + H^+PF_6^-$$
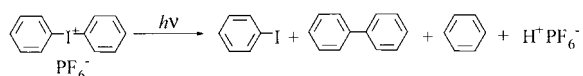
Initiation by protonation[8] proceeds as follows:

$$H^+PF_6^- + O\text{(THF)} \rightleftharpoons HO^+\text{(THF)} \cdot PF_6^-$$
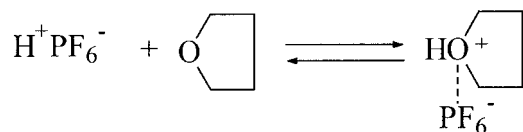
Figure 2 shows time–conversion curves of the polymerization carried out at 30°C. It also shows that the rate of polymerization in the syringe method is much lower than that of the direct polymerization. However, the conversion curve at 30°C is leveled off at around 60% in both polymerizations, indicating that the level-off value is a
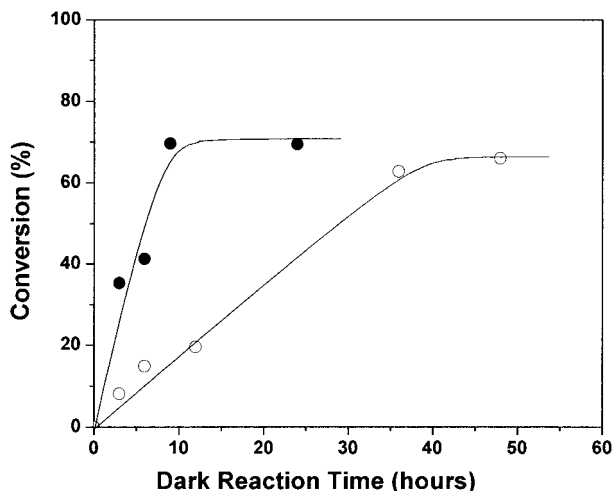

Figure 2 Time–conversion curves of photoinduced cationic polymerization of THF by the (●) direct polymerization method and (○) the syringe method in the presence of 05M initiator and carried out in the dark at 30°C. Photoirradiation for the two methods were carried out under the same conditions at 0°C for 30 min.

function of temperature. It is also a well-known fact that in an exothermic polymerization the equilibrium between propagation and depropagation is shifted toward the direction of depropagation as the temperature increases.[17]

The establishment of an equilibrium between propagation and depropagation[8,17] is as follows:

$$+[OCH_2CH_2CH_2CH_2]_n\text{–}O^+ \cdot PF_6^- + O\text{(THF)} \rightleftharpoons +[OCH_2CH_2CH_2CH_2]_{n+1}\text{–}O^+ \cdot PF_6^-$$
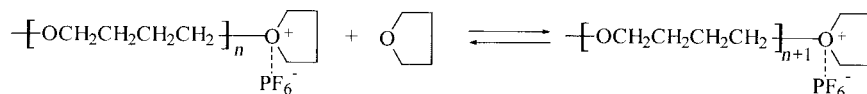
The living nature of the cationic polymerization of THF is due to the stabilization of the propagating cationic species by ion pair formation with the less-nucleophilic complex metal halide anion (PF_6^-) supplied by the initiator.[1–3] However, the cationic propagating species is partially consumed by the attack of basic impurities, which in this case is water. The exposure of the photolytic products to air was unavoidable in the course of syringe transference of the photolytic products of the initiator. The lower rate of polymerization is ascribed to the decreased concentration of the cationic propagating species that is due to the nucleophilic attack of water, which was introduced to the system along with the photolytic products.

Figure 3 shows the relationships between the percentage of conversion and the number-average molecular weight of the resulting polymer in the syringe method carried out at 0°C. The increase in the molecular weight of the resulting polymer with the increase in the percentage of conversion of the polymers having a very narrow molecular weight distribution (polydispersity index, M_w/M_n, = 1.3–1.6) implies the living nature of this polymerization by the syringe method (i.e., the absence of a chain transfer or termination process). The living nature of the system was ascribed to the stabilization of the cationic propagating species by ion pair formation with the less-nucleophilic complex PF_6^- supplied from the initiator.
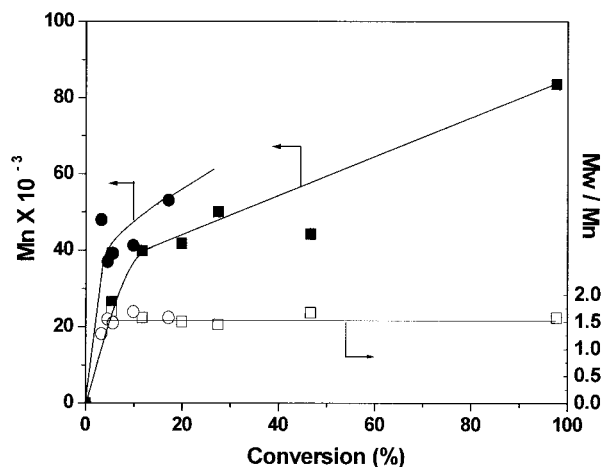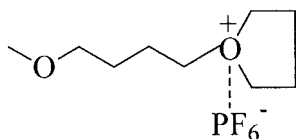
Figure 3 The dependence of the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the resulting polymer on the percentage of conversion in photoinduced cationic polymerization of THF in the presence of $0.05M$ initiator and carried out in the dark at 0°C after photoirradiation at 0°C for 30 min; (●, ○) syringe method and (■, □) direct polymerization method.

Figure 4 The dependence of the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the resulting polymer on the percentage of conversion in photoinduced cationic polymerization of THF in the presence of $0.05M$ initiator and carried out in the dark at 30°C after photoirradiation at 0°C for 30 min; (●, ○) syringe method and (■, □) direct polymerization method.

Stabilization of cationic propagating species by ion pair formation with the less-nucleophilic complex (PF_6^-) is attained as follows[8]:

However, the relationship deviated from linearity; presumably due to the slow initiation, it took more than 10 min for the completion of the photoinitiation.

Meanwhile, a better linear relationship between the two parameters is observed in the polymerization carried out at 30°C until the percentage of conversion reaches a level-off value as shown in Figure 4. It is evident that the molecular weights of the polymers obtained by the syringe method are unexceptionally higher than those obtained by the corresponding direct polymerization method. Furthermore, the molecular weights of
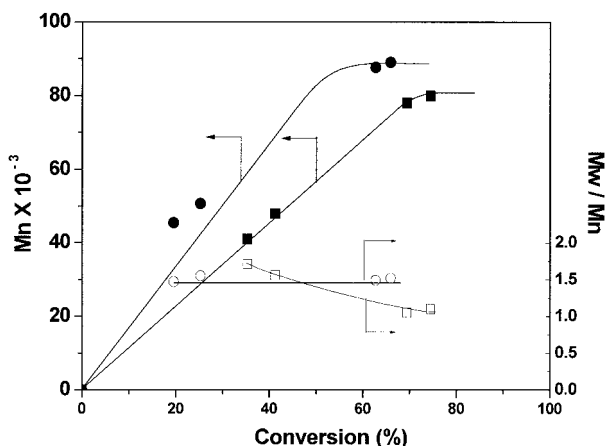
the polymers obtained by the polymerization carried out at a lower temperature are higher than those obtained at a higher temperature.

Considering that the molecular weight of the polymer in the living polymerization is determined by $M = \{[M]_0 - [M]_e\}/[I]_0$, it is plausible that the polymer having a higher molecular weight is obtained from the polymerization carried out at lower temperature, where $[M]_0$, $[M]_e$, and $[I]_0$ are the initial concentration of the monomer, the concentration of the monomer in the equilibrium state, and the initial concentration of the initiator, respectively.

This is supported by the fact that a higher molecular weight polymer is obtained via the syringe method than the corresponding direct polymerization method. The concentration of the living cationic propagating species in the syringe method is lower than that of the direct polymerization method due to the consumption of the cationic species by the reaction with water.

The loss of activity of cationic propagating species due to the reaction with water proceeds according to the following reaction:
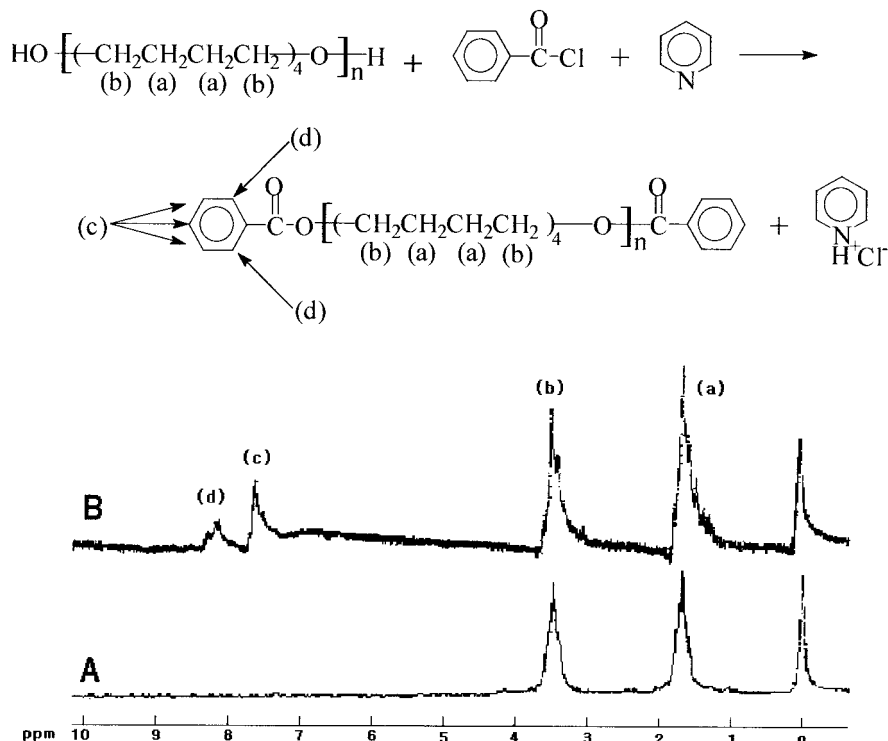
Figure 5 The determination of the functionality of the polymer by a ^{1}H-NMR spectrum of PTHF ($M_n = 3000$) synthesized by the syringe method ($[I] = 0.05M$). Photoirradiation was carried out at 0°C for 30 min, followed by a dark reaction at 30°C: (A) Original sample and (B) benzoylated sample.

In the syringe method systems the contact of the photolytic products with air is unavoidable while the photolytic products are transferred to THF using a syringe. It is therefore postulated that the rate of polymerization and the molecular weight of the polymer obtained by the syringe method approaches that of the direct polymerization, because the duration of the exposure of the photolytic product to air decreases.

Because the polymerization is initiated by the protonation of THF and terminated by the reaction of the cationic propagating center with water, it is expected that the poly(THF) (PTHF) obtained from this system has two hydroxyl groups at both ends. End group analysis was performed by ^{1}H-NMR spectroscopy after converting the hydroxyl end groups to benzoyl groups.[18] Benzoyl chloride (0.1 mL, 9×10^{-4} mol) was added to a 50-mL flask where 1 g of the polymer (3×10^{-4} mol) in 2 mL of pyridine was placed. The mixture was allowed to stand under reflux for 60 min, and then the polymer was precipitated by the addition of 5 mL of sodium hydrogen carbonate followed by filtration and washing with water. The number of func-

tionality was determined by the area ratio of the peak ($a + b$) due to the methylene unit of PTHF and the peak ($c + d$) due to the benzoyl unit of the end group.

$$F = 8(c + d)M_n/5(a + b)M_0$$

where ($a + b$) and ($c + d$) are the peak area due to the methylene proton and aromatic proton of the benzoyl unit, respectively, as shown in Figure 5 and M_n and M_0 are the molecular weight of PTHF and THF, respectively. The values that were very near to 2 reveal that a telechelic PTHF, possessing two hydroxyl groups at both ends, is successfully obtained from this polymerization.

CONCLUSIONS

The living nature of cationic PTHF from less severely dried conditions, which was produced by the addition of the photolytic products of the initiator based on the syringe technique, was inves-

tigated. Although the lower rate of polymerization and polymers having higher molecular weights were obtained by the syringe method compared to those of the corresponding direct polymerization method, it becomes clear that the living nature of the system is still maintained. This suggests the potentiality of this polymerization system for application to the synthesis of a THF-based block copolymer.

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