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Preparation of Methacryloyloxyl Polytetrahydrofuran Macromer

Mikio Takaki, Ryuzo Asami and Tetsuya Kuwabara

Department of Synthetic Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya, 466, Japan

SUMMARY

Methacryloyloxyl polytetrahydrofuran (MA-PTHF) macromer was prepared by the coupling method which involved the reaction of sodium methacrylate with living PTHF. The MA-PTHF macromer obtained by this method was shown to be highly pure macromer by a UV spectrometric method, indicating one vinyl group per molecule. The radical polymerization of the macromer was performed to check the polymerizability of the macromer. At a relatively high concentration of the macromer, it was homopolymerized at a high conversion of ca. 90%. Furthermore, the macromer was quantitatively copolymerized with styrene to the copolymer. This quantitative conversion is consistent with the high purity of MA-PTHF macromer obtained.

INTRODUCTION

For the synthesis of polymer which has a polymerizable group (viz., macromer) by means of living polymerization, two methods have been considered so far. One is based on a coupling reaction of a living polymer with a terminator which contains a vinyl group and the other involves an initiation by a vinyl type of initiator.

In the preparation of PTHF macromer, both the methods mentioned above have been reported. That is, p-vinylbenzyloxyl (ASAMI et al., 1980) and p-vinylphenoxyl (ASAMI et al., 1982) PTHF macromers were prepared according to the former way, and MA-PTHF macromer was synthesized by means of a initiation method (VARGAS et al., 1980) which involved the cationic living polymerization of THF by using methacryloyl hexafluoroantimonate as an unsaturated initiator.

As an alternative method for the preparation of MA-PTHF macromer, we have tried to prepare the macromer according to the following scheme, using reagents such as triethyloxonium tetrafluoroborate (Et_3OBF_4) and sodium metharcylate.

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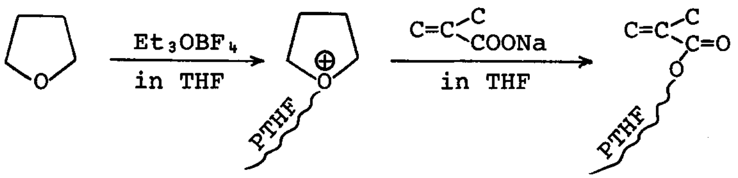

MA-PTHF

The high purity of MA-PTHF thus obtained will be shown in this communication, together with the polymerizability of the macromer.

EXPERIMENTAL

Et$_3$OBF$_4$ was synthesized according to MEERWEIN (1966) by using a high vacuum line. Living PTHF was prepared by the polymerization of THF with Et$_3$OBF$_4$ in THF. Sodium methacrylate was obtained by the reaction of sodium hydroxide with an excess of methacrylic acid in the aqueous solution. The sodium salt obtained was purified by the reprecipitation from methanol into an excess of acetone, ground as fine as possible, and dried in vacuo at room temperature. THF was purified according to the conventional anionic polymerization technique.

The coupling reaction between living PTHF and sodium methacrylate was carried out at 0°C by adding a THF solution of the former into an excess of sodium methacrylate suspension in THF with stirring in a high vacuum system. The reaction mixture was poured into a large amount of methanol/water (3/1, v/v) at 0°C. The precipitated polymer was purified by the reprecipitation from THF into the precipitant, and then freeze-dried. The homo- and copolymerization of MA-PTHF were done by using α,α'-azobisisobutyronitrile (AIBN) at 60°C.

The UV measurment of MA-PTHF was performed in a THF (specially prepared for UV measurement, UVS-82, Nakarai Chemicals LTD.) solution on a double-beam spectrophotometer (Hitachi Model 200-20).

RESULTS AND DISCUSSION

Preparation and Characterization of MA-PTHF

Results of the preparation of MA-PTHF under typical reaction conditions are listed in Table I together with results of the characterization of MA-PTHF obtained. Although in this table only the macromers of the molecular weights of $\approx 8 \times 10^3$ are shown, the molecular weight of the macromer can be controlled by selecting the reaction time of living polymerization of THF. It has been suggested that the conversion of the polymerization of THF should be controlled to be less than 6 wt% (ASAMI et al., 1981) by the polymerization time to prepare MA-PTHF having a very narrow molecular weight distribution. The molecular weight distribution of MA-PTHF prepared under this condition was very narrow as shown in Figure 1 and the value of M_n/M_w was calculated to be 1.10 (Expt M-2) by using a calibration curve obtained with std PTHF.

TABLE I

Preparation and Characterization of MA-PTHF

Expt	Liv. PTHF[a] THF, mL	Liv. PTHF[a] Et_3OBF_4[b] (O^+), mmol	Coupling reac.[c] [ONa]/[O^+][d]	Coupling reac.[c] time, h	Recovered polymer yield,[e] %	Recovered polymer $M_n \times 10^{-3}$ GPC	Recovered polymer $M_n \times 10^{-3}$ VPO (I)	Recovered polymer $M_n \times 10^{-3}$ UV (II)	Recovered polymer MA group/molecule (I/II)
M-1	56	0.266	8.70	15	3.2	9.0	8.0	8.0	1.00
M-2	113	0.515	9.40	38	3.4	9.6	8.0	8.2	0.98

[a] Polymerization temp, 0°C; time, 40 min. [b] In 1,2-dichloroethane ([O^+] = 0.095 mol/L). [c] Reaction temp, 0°C. [d] Mole ratio of $CH_2=C(CH_3)COONa$ to Et_3OBF_4. [e] Wt% against THF charged.

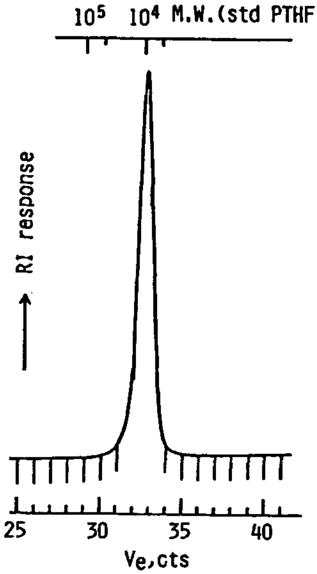

Fig. 1. GPC curve of MA-PTHF obtained in Expt M-2.

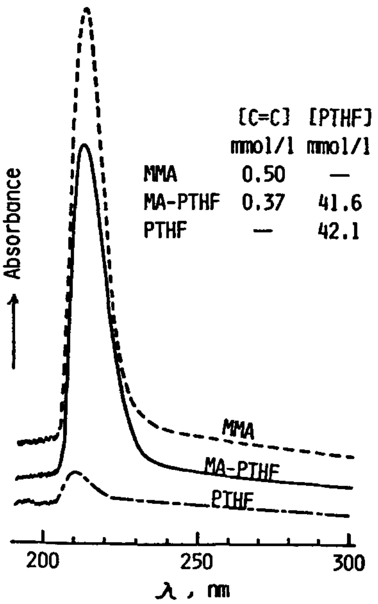

Fig. 2. UV spectra of MMA, MA-PTHF (Expt M-1), and PTHF.

Vargas et al. (1980) claimed that the quantitative analysis of the methacrylic ester function of MA-PTHF by the UV measurement was impossible because the corresponding absorption is located around 200 nm. In this study, however, we could obtain the quantitative data from reproducible UV spectra of the macromer in the THF solution (Figure 2), using a double-beam spectrophotometer and the molar extinction coefficient of methyl methacrylate (MMA) as a model compound ($\varepsilon_{max} = 8.1 \times 10^3$ L mol^{-1} cm^{-1} at $\lambda_{max} = 209$ nm in THF). That is, the molecular weights which were determined by this UV method were in good agreement with those by a vapor pressure osmometric method as demonstrated in Table I.

Polymerizability of MA-PTHF

It was also reported that the homopolymerization of the MA-PTHF macromer prepared by the initiation method was difficult and merely formed the oligomer (VARGAS et al., 1981), although the detailed data were not shown there. However, we have found that the MA-PTHF macromer prepared by the coupling method could highly be homopolymerized as shown in Table II, and it is considered that the polymerizability of MA-PTHF is rather higher than those of p-vinylbenzyloxyl and p-vinylphenoxyl PTHF

TABLE II

Homopolymerization of MA-PTHF[a]

Expt	MA-PTHF [C=C], mmol/L	AIBN mmol/L	Conversion, % UV	Conversion, % GPC	D.P.[b]
H-1	74	8.0	86	88	29
H-2	76	40	86	92	22
H-3	55	57	83	89	9

[a] In benzene at 60°C for 24 h. [b] Degree of polymerization by a GPC calibration curve of linear std PTHF.

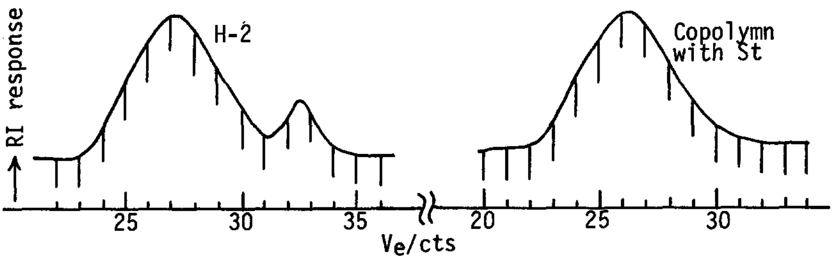

Fig. 3. GPC curves of the polymers obtained in Expt H-2 (in Table II) and in the copolymerization with styrene. The copolymerization conditions are shown in the text.

macromers which have been already reported. For example, at the high concentration of MA-PTHF in Expt H-2, MA-PTHF was polymerized at a conversion as high as ca. 90% and the degree of polymerization of poly(MA-PTHF) went up to 22 (Table II and Figure 3) whereas the conversion of p-vinylbenzyloxyl PTHF to poly(macromer) was 70% under the same conditions (ASAMI et al., 1980). Moreover, Figure 3 shows that in the copolymerization with styrene in bulk, MA-PTHF was quantitatively polymerized under the following conditions: MA-PTHF, 200 mg; styrene, 203 mg; AIBN, 2.6 mg; polymerization temp, 60°C; time, 24 h. This quantitative conversion of the macromer in the copolymerization proves that the purity of MA-PTHF is inherently very high, and this result also confirms the reliability of the UV analyses of the MA-PTHF macromers. Now, it remains in question that the MA-PTHF macromer prepared by the termination method in this communication does polymerize whereas the MA-PTHF macromer by the initiation method (VARGAS et al., 1981) was hardly polymerized by radical initiator although both the macromers seem to be the same structure except for the other end group, i.e., the former is ethoxide whereas the latter is phenoxide.

In addition, it was found that the MA-PTHF macromer could be polymerized by photoinitiation. Further studies on the characteristic behavior of the polymerization and the photopolymerization of the macromer are in progress now.

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