# Investigation of the End Groups of Prepolymers/Macromonomers Prepared by Radical Chain Transfer Reaction

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ABSTRACT: The end-group analysis both for PMMA prepolymers having a carboxyl end group prepared by radical chain transfer reaction and for the macromonomers derived from the above prepolymers was carried out by using size exclusion chromatography (SEC), titration, $^1$H NMR, and high-resolution pyrolysis–gas chromatography (PyGC). The PMMA prepolymers were prepared by the radical polymerization of methyl methacrylate (MMA) with azobis(isobutyronitrile) (AIBN) in benzene at 60 °C in the presence of thioglycolic acid (TGA). Conversion of the prepolymers to the macromonomers was carried out by reaction of the carboxyl end group with glycidyl methacrylate in xylene at 140 °C. The degrees of polymerization ($P_n$) of the prepolymers and the corresponding macromonomers were evaluated on the basis of the end functional group by each method. The chain-transfer constants ($C_s$) of TGA were also determined. $P_n$ values determined by titration, PyGC, and $^1$H NMR were consistent with that determined by SEC with the consideration of the fraction of the initiator residue at the chain end. The fraction of the initiator residue at the chain end was evaluated by PyGC and compared with that evaluated by SEC and polymerization data. It was found that these are in good agreement with each other. From these results, the preparation conditions for the prepolymer and the corresponding macromonomer having high end-group functionality were discussed.

## Introduction

In recent years, research on macromonomers has been actively increasing, and various kinds of macromonomers have been synthesized by radical,[1-3] anionic,[4-9] and cationic[10,11] polymerizations and other methods.[12-14] Preparation of macromonomers by radical chain transfer reaction has been one of the most convenient and hence widely employed methods since it was used in preparation of stabilizers for dispersion polymerizations more than 10 years ago.[15] In preparation of prepolymers and macromonomers, accurate determination of the end-group functionality is important to confirm the introduction of the end functional group and to use them in the preparation of well-defined graft copolymers and other functional polymers. The precise value of the end-group functionality is also necessary to investigate the homopolymerization as well as copolymerization reactivity of macromonomers.[7,8,13b,16] Moreover, study of the polymer chain end provides very useful information for understanding the initiation and termination mechanisms in radical polymerizations. However, accurate determination of the end groups is not necessarily easy and has not been extensively studied because of the very low concentration of the end groups.

For the analysis of the polymer chain end, NMR spectroscopic investigation with isotopic labeling of the end groups has come to be utilized due to recent developments in NMR instruments. For example, the initiator-derived residues in polystyrenes prepared with azobis(isobutyronitrile-$\alpha$-$^{13}C$) was investigated by Moad et al.,[17] and the relative rate of addition of styrene and acrylonitrile to 1-phenylethyl radical using 1,1′-azobis(1-phenyl-[1-$^{13}$C]ethane) was investigated by Tirrell et al.[18] by means of $^{13}$C NMR. Furthermore, Hatada et al. reported the fraction of the cyanoisopropyl end group in radical polymerization with AIBN by using the totally deuterated monomer technique with $^1$H NMR spectroscopy.[19] On the other hand, high-resolution pyrolysis–gas chromatography (PyGC) has also been applied to the analysis of the polymer end group by Tsuge and Ohtani et al.[20]

In this paper, SEC, titration, $^1$H NMR, and PyGC were applied to the analysis of the end groups of prepolymers prepared by the radical chain transfer reaction with thioglycolic acid and the corresponding macromonomers. The results obtained were compared and discussed in terms of the end-group functionality and the chain-transfer constant on the basis of polymerization data.

## Experimental Section

Methyl methacrylate (MMA) was polymerized with $\alpha,\alpha'$-azobis(isobutyronitrile) (AIBN) in benzene at 60 °C for 30 min in the presence of different amounts of thioglycolic acid (TGA) to obtain MMA prepolymers having a carboxyl group at one end. Conversion of each run was 12–15%. The prepolymers were converted to macromonomers by the reaction of the terminal carboxylic acid with glycidyl methacrylate (GMA) in xylene at 140 °C for 6 h in the presence of a small amount of hydroquinone and *N,N*-dimethyllaurylamine as follows:[1]

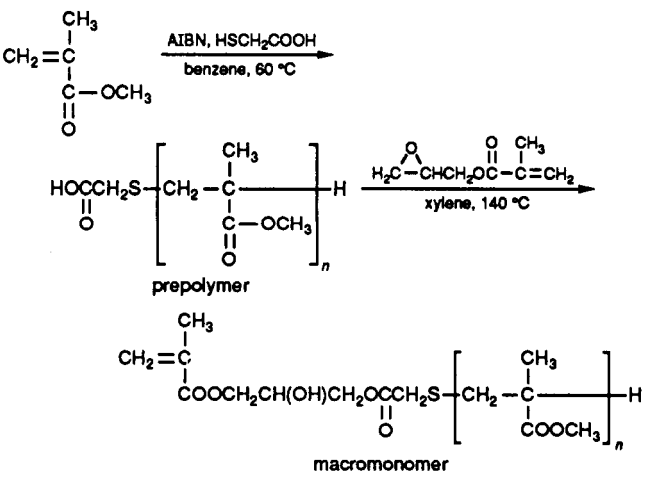


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**Table I**
**Polymerization of MMA with AIBN in the Presence of Thioglycolic Acid as a Radical Chain-Transfer Agent[a]**

| run | feed,[b] mol/L [M] | [S] | [I] | [S]/[M] × 10² | X,[c] % | SEC $M_n$ | SEC $P_n$ | titration[d] $P_n$ | PyGC[d] $P_n$ | PyGC[d] $P_n$[e] | $^1$H NMR[d] $P_n$[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.498 | 0.350 | 0.045 | 7.781 | 15.1 | 2700 | 26 | 26 (25) | 21 (20) | 30 (28) | 29 (28) |
| 2 | 4.507 | 0.100 | 0.045 | 2.219 | 12.3 | 7400 | 73 | 79 (71) | 73 (62) | 91 (73) | 113 (101) |
| 3 | 4.498 | 0.030 | 0.045 | 0.667 | 14.7 | 19000 | 189 | 306 (224) | 198 (144) | 359 (201) | 292 (214) |
| | | | | | $C_s$[f] | | 0.47 | 0.49[g] | 0.61[g] | | |

[a] Polymerizations were carried out with AIBN in benzene at 60 °C. Polymerization time was 30 min in each run. [b] [M], [S], and [I] are the concentrations of MMA, TGA, and AIBN, respectively. [c] X = conversion. [d] The values in parentheses are $P_n$ values corrected by the fraction of the cyanoisopropyl end group using $P_n/P_{n,0}$ values in Table III. [e] $P_n$ determined after the conversion to the corresponding macromonomer. [f] Chain-transfer constant for TGA. [g] Calculated from $P_n$ values in parentheses.

**Table II**
**Conversion of Prepolymers to Macromonomers[a]**

| run | feed, mg prepolymer | feed, mg GMA[c] | conversion[b] $P_{n,tit}$(Prp)/$P_{n,NMR}$(Mac) |
|---|---|---|---|
| 1 | 400.3 | 43.6 | 0.90 |
| 2 | 400.0 | 16.4 | 0.70 |
| 3 | 399.6 | 6.1 | 1.00 |

[a] Reactions of prepolymers with GMA were carried out by adding 6.0 mg of *N,N*-dimethyllaurylamine and 2 mol % of hydroquinone to prepolymers in 1.6 g of xylene (reaction time, 6 h; reaction temperature, 140 °C). [b] Estimated with the degree of polymerization of prepolymer to that of macromonomer using uncorrected $P_n$ values with the fraction of the cyanoisopropyl end group. Prp = prepolymer, Mac = macromonomer. [c] Glycidyl methacrylate.

The obtained prepolymer solutions were precipitated into a large amount of petroleum ether, and the reprecipitation runs were repeated 3 or 4 times to remove the unreacted TGA, AIBN, and MMA. The thus-purified samples were freeze-dried from benzene followed by further drying under vacuum at 50 °C for 2 days. Also, macromonomers were purified by the same precipitation procedures mentioned above. The preparation conditions and the degree of polymerization ($P_n$) of the prepolymers and the corresponding macromonomers are shown in Tables I and II. $P_n$ was determined by size exclusion chromatography (SEC, or gel permeation chromatography (GPC)), titration, PyGC, and $^1$H NMR.

SEC measurements were carried out with a high-speed liquid chromatograph (HLC-802A, Tosoh Co. Ltd.) that was operated with Tosoh G5000H-G3000H columns at 30 °C on chloroform. The molecular weights and $P_n$ were calculated from a polystyrene standards calibration curve. Titrations were carried out with sodium methoxide in acetone with a TSB-10A autoburet and TSC-10A autotitrator (Touadenpa Kogyo Co. Ltd.). The inflection points of the titration curves were used as the neutralization point, from which the end carboxyl contents were calculated. Phenolphthalein was also added as an indicator to confirm the neutralization point. $^1$H NMR spectra were taken with a Varian Gemini-200 (200 MHz) at room temperature in deuterated chloroform. $P_n$ obtained from $^1$H NMR was calculated from the peak intensity ratio of the methoxy protons of the MMA units to the vinyl protons of the end groups of the macromonomers.

Pyrograms were taken with a vertical microfurnance-type pyrolyzer (Yanagimoto GP-1018) directly attached to a gas chromatograph (Shimadzu GC-7A) with a flame ionization detector (FID) and a flame photometric detector (FPD) or to a gas chromatograph (Hewlett-Packard Model 5890A) with an FID and a nitrogen–phosphorus detector (NPD).[20] For the analysis of the sulfur-containing end groups with FID and FPD, weighed polymer samples (ca. 0.5 mg) with ca. 0.01 mg of benzothiophene as an internal standard were pyrolyzed at 700 °C under a flow of helium carrier gas (40 mL/min).[20d,21] For the analysis of the nitrogen-containing end group with NPD and FID, polymer samples were pyrolyzed at 460 °C.[20d] A fused-silica capillary column (50 m × 0.2 mm i.d.) coated with poly(dimethylsiloxane) (0.33 μm thick) immobilized through chemical cross-linking was used. The 40 mL/min carrier gas flow rate at the pyrolyzer was reduced to 0.7 mL/min at the capillary column by a splitter. The column temperature was initially set at 0 °C by using a $CO_2$ cooling unit for the FPD mode and at 40 °C for the NPD mode and then programmed to 250 °C at the rate of 4 °C/min. Identification of the peaks on the pyrograms was carried out by using a gas chromatograph–mass spectrometer (Shimadzu QP-1000) directly attached to the pyrolyzer.

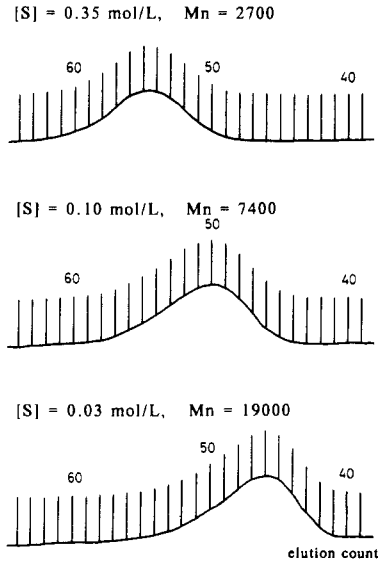


**Figure 1.** SEC curves of the radical polymerization products of MMA in the presence of different amounts of thioglycolic acid as a chain-transfer agent. SEC was taken on chloroform at 30 °C. Flow rate was 1.2 mL/min. One elution count was ca. 1 mL.

## Results and Discussion

**Degree of Polymerization on the Basis of the End Group.** Figure 1 shows SEC curves of the prepolymers (runs 1–3) taken with a RI detector at 30 °C where the feed monomer concentrations were fixed at [M] = 4.5 mol/L and the concentration of TGA, [S], increased from 0.03 to 0.35 mol/L. It is seen in Figure 1 that the elution count at the peak maximum shifts in the direction of lower molecular weight as [S]/[M] increases, as is known, indicating that TGA plays a role as both a molecular weight modifier and a carrier for the terminal carboxyl group. The number average molecular weight ($M_n$) determined from SEC and the corresponding $P_n$ are shown in Table I. In the case of poly(methyl methacrylate) (PMMA) polymerized without TGA ([S] = 0), $M_n$ determined by SEC was 70.4 × 10³ under the same polymerization conditions ([MMA] = 4.5 mol/L and [AIBN] = 0.045 mol/L at 60 °C in benzene).

$P_n$ values of the prepolymers obtained by the titration of the end carboxyl group are also shown in Table I. It was difficult to determine $P_n$ of the prepolymers by $^1$H NMR, and $P_n$ by $^1$H NMR in Table I was obtained for macromonomers using the peak intensity ratio of the methoxy protons to the vinyl protons of the end group. These $P_n$ values determined by titration and $^1$H NMR correspond

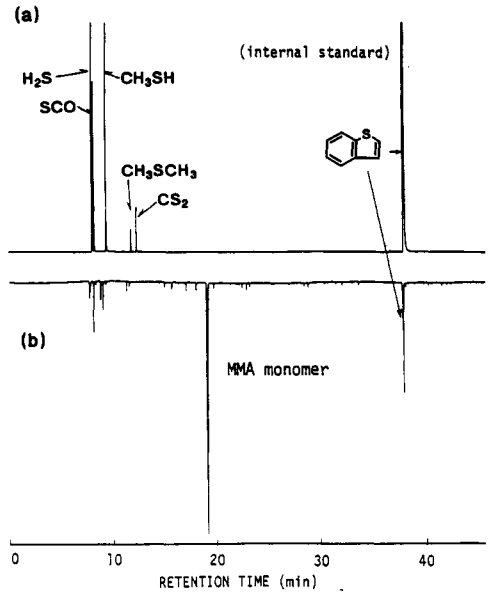


**Figure 2.** Pyrograms of the PMMA prepolymer having a (carboxymethyl)thio group (run 1) taken at 700 °C (a) with a sulfur-specific FPD and (b) with a FID.

to the number of MMA monomer units per residue of the chain-transfer agent at the chain end, while $P_n$ obtained by SEC corresponds to the number of monomer units per all types of end groups. Conversions of the prepolymers to the corresponding macromonomers were carried out under the conditions shown in Table II.

Figure 2 shows the pyrograms at 700 °C for the prepolymer (run 1) simultaneously taken with a sulfur-specific FPD (a) and an ordinary FID (b). It can be seen in Figure 2b that there are many minor peaks together with two strong peaks corresponding to MMA monomer and benzothiophene added as an internal standard in the pyrogram. PMMA main chains are almost quantitatively depolymerized to monomers under the given PyGC conditions. However, it is difficult to discriminate the sulfur-containing minor pyrolysis products derived from the chain-transfer agent residue at the chain end of the prepolymer. They can, however, be selectively observed as five main peaks corresponding to $H_2S$, $CH_3SH$, SCO, $CS_2$, and $CH_3SCH_3$ with the sulfur-specific FPD in Figure 2a in addition to the isolated single peak of benzothiophene. Therefore, the relative amounts of $HOOCCH_2S$ at the chain end to those of MMA units ($RA_S$) in the prepolymer samples can be estimated from the relation between the peak intensities of the five main peaks in the FPD mode and that of MMA in the FID and NPD modes after normalization with those of benzothiophene. The relative amounts of the functional end groups in the corresponding macromonomers can be estimated in basically the same way. The $P_n$ of the prepolymers corresponding to the number of MMA monomer units per $HOOCCH_2S$ end group is given by $(RA_s)^{-1}$ and is shown in Table I. This corresponds to the $P_n$ per carboxyl end group obtained by titration.

Pyrograms of the prepolymers were also taken at 460 °C with FID and NPD to get information about the residue of the initiator at the chain end. Among the peaks of the various products, the peaks reflecting the cyanoisopropyl end groups derived from AIBN were assigned by NPD and GC/MS.[20d] By taking the relative peak intensity of these peaks, one can determine the relative amounts of the cyanoisopropyl end groups to MMA units ($RA_N$). The degree of polymerization of the prepolymers and the corresponding macromonomers were calculated by taking into consideration both the $HOOCCH_2S$ group and the cyanoisopropyl group at the chain end as follows:[20d]

$$P_n = 1/(RA_S + RA_N)$$

under the assumption that each polymer molecule has either one cyanoisopropyl or one $HOOCCH_2S$ end group. This assumption will be discussed later. $P_n$ values thus obtained are shown in parentheses in Table I. $P_n$ values determined by titration and $^1H$ NMR were also corrected by the fraction of polymers having only an initiator residue at the chain end using the fraction of cyanoisopropyl end group estimated by SEC in Table IV and are shown in parentheses in Table I. It is seen in Table I that the $P_n$ values in parentheses are in better agreement with $P_n$ values determined by SEC and with each other than $P_n$ values obtained with consideration of the $HOOCCH_2S$ end group alone.

**Table III**
**End-Group Functionality[a]**

| run | prepolymer $(P_{n,SEC}/P_{n,tit})$ | prepolymer $(P_{n,SEC}/P_{n,PyGC})$ | macromonomer $(P_{n,SEC}/P_{n,NMR})$ |
|---|---|---|---|
| 1 | 1.00 | 1.00 | 0.90 |
| 2 | 0.92 | 1.00 | 0.65 |
| 3 | 0.62 | 0.95 | 0.65 |

[a] Estimated from the ratio of $P_n$ determined by SEC to that obtained by titration, NMR, and PyGC with the consideration of only $HOOCCH_2S$ end groups (number of MMA monomer units per $HOOCCH_2S$ end group).

The degree of conversion of the prepolymer to the corresponding macromonomer can be estimated from the ratio of the number of MMA monomer units per $HOOCCH_2S$ end group to that per polymerizable end group of the macromonomer using $P_n$ in Table I. These are shown in Table II. It is seen that the prepolymers were converted to the macromomers with high yield except for run 2. The reason for the low conversion of run 2 is not clear. $P_n$ values obtained by PyGC for the prepolymers and the corresponding macromonomers must be equal in Table I since $P_n$ values were determined on the basis of the sulfur-containing pyrolysis products for both the prepolymers and the macromonomers. The difference in Table I is probably related to the existence of unassigned pyrolysis products from the polymerizable end group of the macromonomers due to the more complex pyrogram for the macromonomer, which requires further study.

For the radical polymerization of vinyl monomers in the presence of the chain-transfer agent, $P_n$ of the formed polymer is related to the kinetic data as follows:[22]

$$\frac{1}{P_n} = \frac{k_t R_p}{k_p^2[M]^2} + C_s\frac{[S]}{[M]} + C_m + C_i\frac{k_t R_p^2}{k_p^2 f k_d[M]^3}$$

$$= \frac{k_t R_p}{k_p^2[M]^2} + C_s\frac{[S]}{[M]} \quad (\text{for } C_m \approx 0, C_i \approx 0) \quad (1)$$

$$= \frac{1}{P_{n,0}} + C_s\frac{[S]}{[M]} \quad (2)$$

where $P_{n,0}$ is the $P_n$ of PMMA polymerized without TGA ([S] = 0) and is equal to $(k_t R_p/k_p^2[M]^2)^{-1}$. $R_p$ is the polymerization rate, $C_s$, $C_m$, and $C_i$ are the chain-transfer constants to TGA, MMA, and AIBN, respectively, and $k_p$ and $k_t$ are the rate constants for the propagation and termination reactions. The chain-transfer constants for initiator, monomer, and polymer are $C_{AIBN} = 0$, $C_{MMA} = 0.07 \times 10^{-4}$–$0.18 \times 10^{-4}$, and $C_{PMMA} = 0.1 \times 10^{-4}$–$0.21 \times 10^{-4}$,[24] which are negligibly small compared with that of

Table IV
**Estimation of the Fraction of the Cyanoisopropyl End Group at the PMMA Chain End Polymerized with AIBN in the Presence of Thioglycolic Acid[a]**

| run | [M], mol/L | $1/P_n$[b] | $R_p \times 10^4$, mol/L·s | $k_tR_p/k_p^2[M]^2 \times 10^3$ | fraction, % | | |
|---|---|---|---|---|---|---|---|
| | | | | | $P_n/P_{n,0}$[c] | kinetic data[d] | PyGC[e] |
| 1 | 4.498 | 0.0385 | 3.77 | 1.79 | 3.7 | 4.7 | 5.9 |
| 2 | 4.507 | 0.0137 | 3.08 | 1.46 | 10.4 | 10.7 | 15.6 |
| 3 | 4.498 | 0.00529 | 3.67 | 1.74 | 26.8 | 32.9 | 27.2 |

[a] Polymerization time was 30 min. [b] Determined by SEC using a PSt standards calibration curve. [c] $(P_n/P_{n,0}) \times 100$ using $P_{n,0}^{-1} = 1.42 \times 10^{-3}$ determined by SEC for PMMA polymerized with [S] = 0 ($M_n$ was 70 400 as the average of four times of polymerization). [d] Calculated from $(P_nk_tR_p/k_p^2[M]^2)$ using $R_p$ in the table with $k_p = 5.15 \times 10^2$ and $k_t = 2.55 \times 10^7$ L/mol·s.[24] [e] Determined by using $RA_S$ and $RA_N$ in the text.

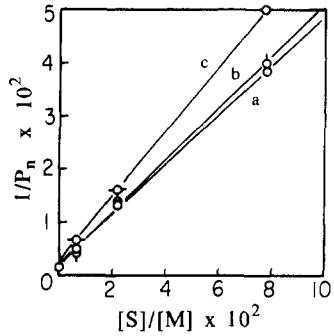


**Figure 3.** $1/P_n$ versus [S]/[M] plots. $P_n$ for prepolymers determined from SEC (O, a), titration (O, b), and PyGC (O, c). Straight lines were drawn by least-squares fitting the data.

TGA. The chain-transfer constant for benzene is $C_{Bz} = 0.018 \times 10^{-4}$–$1.92 \times 10^{-4}$ and is negligible, too. Hence, $C_m \approx 0$ and $C_i \approx 0$ are safely assumed in this work.

Figure 3 shows $1/P_n$ versus [S]/[M] relationships of the prepolymers determined from the three different methods; the slope of each line gives the chain-transfer constants $C_s$ through eq 2. The $C_s$ values are shown in Table I. It is seen in Figure 3 that the $1/P_n$ versus [S]/[M] relationships by SEC, titration, and PyGC are linear and very close to one another. $C_s$ is 0.47 from SEC, 0.49 from titration, and 0.61 from PyGC. In regard to $C_s$ of thiol compounds, Roy et al. applied the dye technique to determine $C_s$ in the radical polymerization of MMA.[23] They obtained $C_s = 0.43$ for TGA by the dye technique and 0.44 by the viscosity method. $C_s$ of TGA in the radical polymerization of MMA was obtained as 0.63–0.75 and 0.5 at 60 °C in the preparation of MMA macromonomers by the radical chain transfer method in our previous reports.[1b,c] The values obtained in the present work are consistent with those of the previous reports.

**Fraction of Initiator Residue and End-Group Functionality.** If the assumption that all polymer molecules have either one cyanoisopropyl end group or one carboxyl end group is valid with good approximation in this work, the fraction of the cyanoisopropyl end group at the polymer chain end evaluated from PyGC by using this assumption[20d] should be consistent with that calculated from the ratio $(P_n/P_{n,0})$ or $(P_nk_tR_p/k_p^2[M]^2)$ from the polymerization data, where $P_{n,0}$ is the $P_n$ of the polymerization product without TGA. The $P_n$ of PMMA obtained in the absence of TGA was 704 under the same polymerization conditions. The values calculated from the polymerization data were compared with those obtained from PyGC and are shown in Table IV. $(P_nk_tR_p/k_p^2[M]^2)$ was calculated by using $R_p$ in Table IV and $k_p = 5.15 \times 10^2$ and $k_t = 2.55 \times 10^7$ (L/mol·s).[24]

The values obtained from the polymerization data for runs 1–3 in Table IV are consistent with those obtained by PyGC. This indicates that the assumption used for the determination of $P_n$ by PyGC is approximately valid for our polymerization systems. This means that when MMA is polymerized with AIBN in the presence of TGA, the primary radical adds to MMA monomer to initiate the polymerization and then the propagating radical abstracts hydrogen from TGA. Thus-formed TGA radical reinitiates the polymerization. During these processes, other types of chain-transfer reactions, such as chain-transfer reactions to initiator, monomer, solvent, and polymer chain, do not give a significant contribution, as expected from the small values of $C_s$ for these chain transfers. It is also well-known that termination by disproportionation reaction is predominant in the radical polymerization of MMA. Hatada et al. investigated the fraction of the cyanoisopropyl end groups of PMMA prepared by radical polymerization with AIBN by NMR and concluded that 85% of the polymer molecules were terminated by the disproportionation reaction.[19] This fact suggests that formation of polymer molecules having two cyanoisopropyl groups or two (carboxymethyl)thio groups at both chain ends should be minor in our polymerization system.[25]

The end-group functionality of prepolymers and the corresponding macromonomers can be estimated by taking the ratio of $P_n$ determined by SEC to $P_n$ corresponding to the number of MMA monomer units per $HOOCCH_2S$ group obtained by titration, NMR, and PyGC. The end-group functionalities thus obtained are shown in Table III. It is seen in Table III that the end-group functionality of the prepolymers decreases from run 1 to run 3 as [S]/[M] decreases. Especially, the end-group functionality of run 3 is considerably low. The low end-group functionality for the macromonomer of run 2 is the result of low conversion of the prepolymer to the macromonomer as seen in Table II. These situations can also be seen in Table IV, where the fraction of the end carboxyl groups decreases as [S]/[M] decreases and the fraction of initiator fragment at the chain end becomes considerable (about 30%) at [S]/[M] = 0.03 even at the low conversion. In this case, macromonomers having high end functionality cannot be produced. It is also seen that the end-group functionality of the prepolymers obtained at [S]/[M] = 0.35 can be greater than 95%. In this case, the corresponding macromonomer with high end-group functionality can be obtained as seen in Tables II and III. This indicates that the prepolymers and the corresponding macromonomers having high terminal functionality can be obtained by the radical chain-transfer method with a constant amount of sufficient chain-transfer agent, which can be realized by the continuous addition of a constant amount of the chain-transfer agent into the polymerization system.

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