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ORIGINAL CONTRIBUTION

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Control of polymer structure by a chain-transfer reaction in the radical polymerization of acrylamide by *β*-mercaptopropionic acid and 1,2,6-hexanetriol trithioglycolate

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Abstract Star polymer synthesis by radical polymerization of acrylamide (AM) in the presence of thiol compounds was investigated. When 1,2,6-hexanetriol trithioglycolate (HTTG), as a trithiol compound, was used the molecular weights of the polymers were about 3 times those obtained in the presence of *β*-mercaptopropionic acid, as a monothiol compound, at the same concentration of thiol compounds in the feed. From viscosity measurements of the polymers and analysis of the ^{1}H NMR spectra of the polymers, we presumed that a star-shaped polymer of AM could be synthesized by radical polymerization in the presence of HTTG.

Key words Acrylamide · 1,2,6-Hexanetriol trithioglycolate · Radical polymerization · Star-shaped polymer · *β*-Mercaptopropionic acid

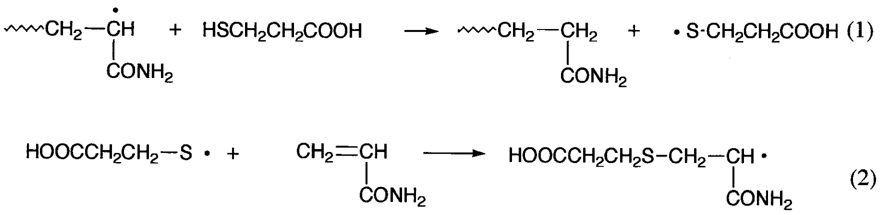
Introduction

It is known that a water-soluble polymer of acrylamide (AM) with high molecular weight can be used as a polymer flocculant and a paper strength resin, but such a polymer in aqueous solution has a very high viscosity, which limits its uses. Branched water-soluble polymers make it possible to decrease the viscosity of the polymer solution in water, since the hydrodynamic radius of a branched polymer is lower than that of corresponding linear polymers with the same molecular weight [1]. Namely, water-soluble star polymers with high molecular weights seem to be very useful to use in a high concentration.

Recently, the macromolecular architecture has been well developed. Many methods are now available for synthesizing various types of branched polymers, such as star-shaped polymers [2–8], hyperbranched polymers [9–12] and dendrimers [13–16]. The molecular properties of these materials are reported to be clearly different from their linear analogues. Among branched polymers, star-shaped polymers with three arms were synthesized by using trifunctional initiators of anionic, cationic and radical polymerization [2].

In radical polymerizations, it is well known that thiol compounds are useful chain-transfer reagents, and the fragment of the chain-transfer reagent is introduced to the chain end of the polymer formed. When we use trithiol compounds as chain-transfer reagents, it is possible to produce a star-shaped polymer, if chain-transfer reactions occur at all the SH groups of the trithiol compounds. This method may provide a convenient method of synthesis of star polymers. Nevertheless, star polymer synthesis using trithiol compounds in radical polymerization of AM has not been reported to our knowledge in the literature.

To explore the possibility of the synthesis of a star-shaped polymer of AM by radical polymerization, trithiol compounds were used as chain-transfer reagents. For this purpose, we selected 1,2,6-hexanetriol trithioglycolate (HTTG), as a trithiol compound, and investigated the radical polymerization of AM with 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of HTTG (Fig. 1). The radical polymerization of AM in the presence of *β*-mercaptopropionic acid (MPA), as a monothiol compound, was also examined to elucidate the structure of the polymer obtained in the presence of HTTG.



Scheme 1 Chain-transfer reaction to *β*-mercaptopropionic acid (*MPA*) in the radical polymerization of acrylamide (*AM*)

Experimental

Materials

AM (Wako Pure Chemical Co.) was purified by recrystallization from benzene several times. AIBN was used after recrystallization from methanol. Commercially available MPA and HTTG (Tokyo Chemical Industry Co.) were purified by distillation before use. Solvents and other reagents were used after purification by conventional methods.

Polymerization procedure

Polymerization was carried out in a sealed glass tube. After required amounts of reagents had been introduced into the tube, the tube was degassed and then sealed under high vacuum. Polymerization was carried out in a thermostat at a constant temperature for a given time. After polymerization, the tube was opened, and the contents in the tube were poured into an excess of acetone to precipitate the polymer formed. The polymers were washed with a large amount of acetone and dried under high vacuum at room temperature overnight. The polymer yield was calculated by gravimetry.

Characterization of polymers

The viscosity of the polymers in water was measured with a Ubbelohde viscometer at 25 °C. The viscosity-average molecular weight (M_v) of the poly(AM) was calculated using the following equation [17]: $[\eta] = (6.31 \times 10^{-3}) \times M_v^{0.8}$. The number-average molecular weight (M_n) of the polymers was determined by the ratio of the peak area of the methylene proton based on the main chain at 1.6 ppm and the methylene proton (–S–CH$_2$–) derived from HTTG and MPA at 3.4 and 2.6 ppm, respectively. The structure of the polymer was determined by ^{1}H NMR spectroscopy. ^{1}H NMR spectra of the polymers are recorded using a Jeol A-400 NMR in D_2O solvent at 25 °C.

Results and discussion

Polymerization of AM in the presence of MPA

For synthesizing the AM star polymer by using a chain-transfer reaction in radical polymerization, we first examined the radical polymerization of AM in the presence of a monothiol compound because it gives us useful information about the chain-transfer ability of a monothiol compound in the radical polymerization of AM to design a trithiol compound for preparation of the star-shaped polymers with three arms. Many thiol compounds are used as chain-transfer reagents in radical polymerizations to regulate the molecular weight of the resulting polymers. Among them, we chose MPA as a monothiol compound and we conducted the polymerization of AM with AIBN in the presence of MPA at 60 °C. Since the polymerization of AM in methyl alcohol was reported to be faster than that in water [18], the polymerization of AM was performed in methyl alcohol. The results are shown in Table 1. Both the polymer yields and the molecular weight of polymer determined by viscosity measurement decreased with an increase in the amount of charged MPA, suggesting that the addition of the thiyl radical generated by the chain-transfer reaction is slow as compared with that of the propagating radicals. The chain-transfer reaction of the propagating radical to MPA can be written as in Scheme 1.

The relationships between $1/P_n$ and the ratio of the concentrations of MPA and AM as shown in Fig. 2 gave a straight line. From the slope of the line, the chain-transfer constant of MPA (C_{tr}) was determined to be 0.18 using Eq. (1):

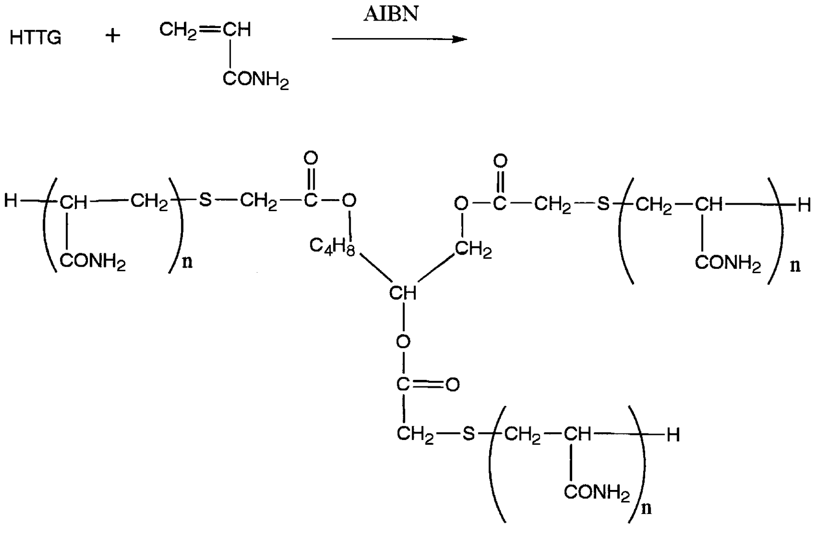
$$1/P_n = C_{tr}[\mathrm{MPA}]/[\mathrm{AM}] + (k_t/k_p^2/[\mathrm{AM}]^2)R_p \ , \qquad (1)$$

where P_n is number-average degree of polymerization, R_p is rate of polymerization, and k_t and k_p are termination and propagation rate constants, respectively. We used AIBN as the initiator, and the polymerization was carried out at constant AIBN and AM

Table 1 Polymerization of acrylamide (*AM*) in methyl alcohol in the presence of *β*-mercaptopropionic acid (*MPA*) at 50 °C for 5 h. Concentration of AM: 1.5 mol/l; concentration of 2,2′-azobis(isobutyronitrile) (*AIBN*): 1.5×10^{-3} mol/l

Number	[MPA] × 10^2 (mol/l)	Yield (%)	$[\eta]$ (dl/g)	$M_v \times 10^{-4}$[a]
1	27.0	56.2	3.61	0.27
2	15.0	63.1	4.57	0.37
3	9.0	73.1	5.90	0.51
4	4.5	72.0	7.74	0.73
5	3.0	85.3	12.0	1.3
6	1.5	87.2	15.2	1.6
7	1.0	89.6	20.8	2.5
8	0.5	89.4	27.1	3.5
9	0.10	85.6	37.8	5.3
10	–	94.6	47.4	7.0

[a] Calculated from $[\eta] = KM_v^a$ ($K = 6.31 \times 10^{-3}$, $a = 0.8$)



Scheme 2 Polymerization of AM in the presence of 1,2,6-hexanetriol trithioglycolate (*HTTG*)

concentrations, i.e., the second term in Eq. (1) was regarded as a constant, so C_{tr} was determined as the slope of the line obtained from the relation between the ratio of the concentrations of MPA and AM] and P_n.

In the radical polymerization of methyl methacrylate (MMA) in the presence of MPA at 50 °C, the chain-transfer constant to MPA was reported to be 0.39 [19]. Thus, the value of the chain-transfer constant to MPA in the polymerization of AM obtained in this study seems to be reasonable. Since the chain-transfer constants to monomer, polymer and methyl alcohol were reported to be 0.61×10^{-4}, 0.6×10^{-4} and 0.13×10^{-4} [20], the results of the polymerization of AM in the presence of MPA indicated that the structure of all the polymer formed has an MPA fragment at the chain end as shown in Scheme 1. This suggests that the star-shaped polymer of AM would be synthesized by selecting an adequate trithiol compound.

Polymerization of AM in the presence of HTTG

For synthesizing a star-shaped polymer of AM by radical polymerization, we selected HTTG as a trithiol chain-transfer reagent, because a study of the chain-transfer reaction of HTTG in the radical polymerization of AM was not found in the literature. In addition to this, the structure of the thiol group of HTTG seems to be similar to that of MPA. So, the polymerization of AM with AIBN in methanol in the presence of HTTG was conducted, and the results are listed in Table 2. The polymer yields and the molecular weights of the polymers were found to decrease with an increase in the HTTG concentration in the feed. The molecular weights of the polymers decreased sharply with an increase in the amount of HTTG compared with those of MPA. Moreover, the molecular weights of the polymers obtained in the presence of HTTG were higher than those obtained in the presence of MPA at the same feed concentration of the thiol compound as shown in Fig. 3, suggesting that three thiol groups of HTTG seem to act as chain-transfer reagents in the polymerization of AM.

If all the thiol groups of HTTG participate in the chain-transfer reaction in the polymerization of AM, a star-shaped polymer with three arms will be synthesized. To elucidate this point, the structure of the polymer obtained in the presence of HTTG was analyzed by ^{1}H NMR spectroscopy.

A typical ^{1}H NMR spectrum of the polymers obtained in the presence of HTTG is shown in Fig. 4. The peaks of the methylene proton based on $-CH_2-S-CH_2-$ derived from HTTG were detected in the ^{1}H NMR spectrum, but the peak based on the thiol protons of HTTG was not observed at 1.3 ppm, which appears in HTTG. Thus, we presumed that the thiol groups of

Table 2 Polymerization of AM with AIBN in methyl alcohol in the presence of 1,2,6-hexanetriol trithioglycolate (*HTTG*) at 50 °C for 5 h. Concentration of AM: 1.5 mol/l; concentration of AIBN: 1.5×10^{-3} mol/l

Number	[HTTG] × 10^2 (mol/l)	Yield (%)	[η] (dl/g)	$M_v \times 10^{-4a}$
1	20.0	40.6	2.04	0.14
2	15.0	45.6	5.91	0.52
3	9.0	53.8	8.38	0.81
4	5.0	69.4	9.29	0.99
5	4.5	60.7	11.0	1.1
6	3.0	64.9	12.3	1.3
7	1.5	78.6	16.9	1.9
8	0.9	84.2	23.3	2.9
9	0.5	87.9	28.9	3.8
10	0.3	93.6	32.4	4.4

[a] Calculated from $[\eta] = KM_v^a$ ($K = 6.31 \times 10^{-3}$, $a = 0.8$)

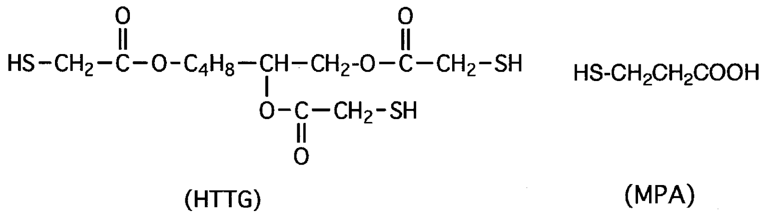


Fig. 1 Chemical structures of MPA and HTTG

HTTG mostly participated in the chain-transfer reaction in the polymerization of AM as shown in Scheme 2, leading to the formation of a star-shaped polymer.

To further confirm the polymer structure, we compared the molecular weights of polymers obtained in the presence of HTTG and MPA. Since MPA has an ethylene spacer between the sulfur and the carbonyl carbon, whereas a methylene spacer is between them in HTTG, the chain-transfer constant of MPA and HTTG is not likely to be the same. However, the chain-transfer constant to MPA and marcaptoacetic acid or its ester was reported to be similar in the radical polymerization of MMA [19]. So, the viscosity-average molecular weight of the polymer obtained in the presence of HTTG ($M_{v},_{\mathrm{HTTG}}$) was compared with that obtained in the presence of MPA ($M_{v,\mathrm{MPA}}$). The relationships between M_v of each polymer and the concentration of the thiol compound in the feed are shown in Fig. 3. $M_{v},_{\mathrm{HTTG}}$ was about 3 times that of $M_{v,\mathrm{MPA}}$ at the same concentration of thiol in the feed under our experimental conditions, suggesting that the star-shaped polymer would be synthesized. However, it is difficult to confirm the synthesis of the star-shaped polymer from a comparison of the M_v of the polymers because the hydrodynamic radius of branched polymers is lower than those of linear polymers. Thus, the M_n determined from the NMR spectra of the polymers was used to compare the molecular weights of the polymers.

The M_n of the polymers obtained at a thiol concentration of MPA $= 1.5 \times 10^{-2}$ mol/l and HTTG $= 0.5 \times 10^{-2}$ mol/l in the feed was determined by the ratio of the peak area of the methylene proton based on the main chain at 1.6 ppm and the methylene proton adjacent to the sulfur atom ($-S-CH_2-$) derived from HTTG and MPA at 3.4 and 2.6 ppm, respectively. The M_ns of the polymers obtained in the presence of MPA and HTTG were determined to be 1.9×10^4 and 6.0×10^4, respectively. Namely, the ratio was about 3 times as large at the same concentration of thiol compound in the feed.

The M_ns determined from the ^{1}H NMR spectra of the polymers obtained at different thiol concentrations were plotted against [η], and the results are shown in Fig. 5. At lower M_n of the polymers obtained in the presence of HGGT, the line was almost the same as that obtained in the presence of MPA, which gave a straight line regardless of the molecular weight. However, the line obtained in the presence of HTTG was found to

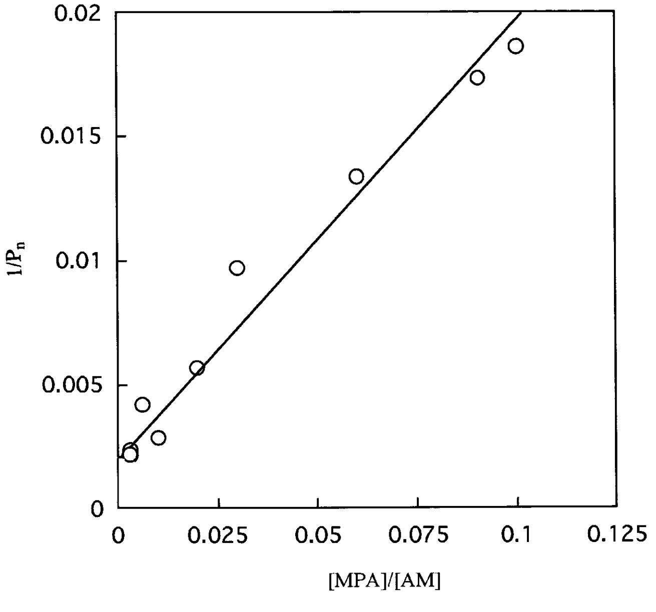


Fig. 2 Relationships between $1/P_n$ and [MPA]/[AM] in the polymerization of AM

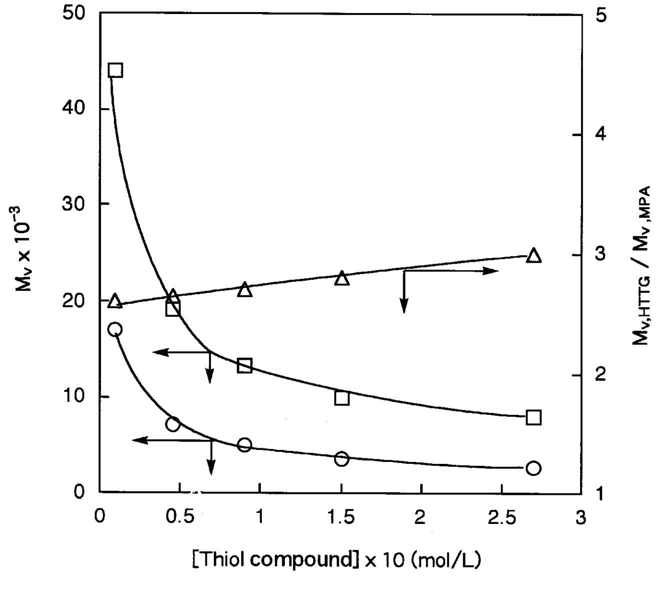


Fig. 3 Relationships between the concentration of the thiol group and M_v of the polymer obtained in the presence of HTTG (□) and MPA (○)

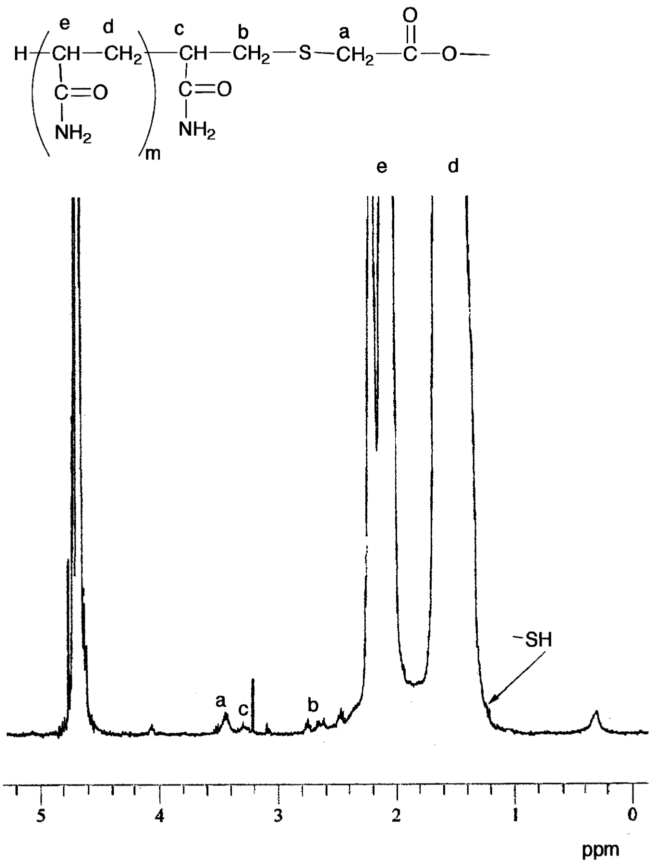


Fig. 4 ^{1}H NMR spectrum of the polymer obtained from the polymerization of AM with AIBN in methyl alcohol at 50 °C in the presence of HTTG

deviate from the straight line. This is likely to be due to the difference in the hydrodynamic radius of the polymers, since its effect becomes much larger with increasing molecular weight of the polymers [1]. This indicates that the product obtained from the polymerization of AM in the presence of HTTG consists of a star-shaped polymer.

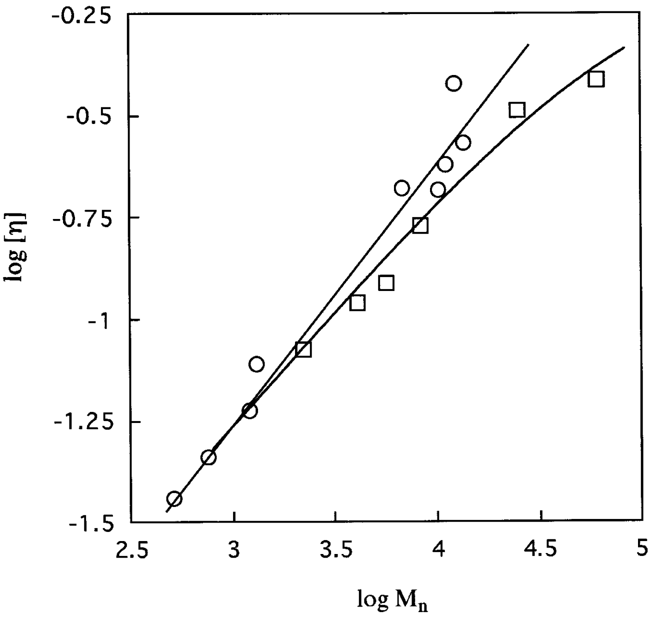


Fig. 5 Relationships between [*η*] and M_n obtained from polymerization of AM in the presence of HTTG (□) and MPA (○)

So far as using chain-transfer reaction in radical polymerization for synthesizing star-shaped polymers is concerned, it is difficult to avoid undesirable reactions, such as chain transfer to monomer, polymer and solvent, and termination between the propagating radical leading to a decrease in the content of star-shaped polymer. Although we did not determine the contents of linear and star-shaped polymers, the polymers obtained in the presence of HTTG seem to be mostly of star-shaped structure as determined from the NMR spectra and the comparison of the M_n of the polymers.

Conclusion

The chain-transfer constant of MPA, as a monothiol compound, was determined to be 0.18. When HTTG, as a trithiol compound, was used, the molecular weights of the polymers were about 3 times those obtained in the presence of MPA at the same concentration of thiol compounds. From analysis of the ^{1}H NMR spectra and the molecular weights of the polymers, it was found that all the thiol groups in HTTG participate in the polymerization.

We can demonstrate that the synthesis of a star-shaped polymer of AM is possible by radical polymerization in the presence of HTTG, although other structures of the polymers besides star-shaped polymers are not excluded.

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