

Synthesis and Characterization of Novel Polymers Containing Sulfur from 3-Mercaptopropionic Acid

Yong-Kyung LEE, Kenjiro ONIMURA, Hiromori TSUTSUMI, and Tsutomu OISHI[†]

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi, 755-8611 Japan

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ABSTRACT: Three new monomers, 2-hydroxyethoxycarbonylethyl methoxycarbonylethyl sulfide (HEMS), 2-hydroxyethoxycarbonyl (2'-methyl) ethyl methoxycarbonylethyl sulfide (HMMS), and 3,3'-dithiodiethylcarboxy allyl (DTCA) were synthesized from 3-mercaptopropionic acid (3-MPA) or methyl 3-mercaptopropionate (M3-MP). Polycondensations of HEMS and HMMS were performed with several metal acetates as catalysts to obtain the corresponding polythioethers with number average molecular weights (M_n) of up to 6.4×10^3 . Radical polymerizations of DTCA were carried out in bulk at 110°C to obtain polymers having allyl groups in the side chain. Polymerizations of DTCA with ethylene diamine (EDA) or hexamethylene diamine (HDA) were performed under various conditions to obtain the corresponding polymers. Decomposition temperatures (T_d) and glass transition temperatures (T_g) of the polymers were 146–252°C and -54 – -1 °C, respectively. Crystallinity of the polymers obtained by polymerizations of DTCA with EDA and HDA was 25–49%.

KEY WORDS Polycondensation / 3-Mercaptopropionic Acid / Thioether / Disulfide / Glass Transition Temperature / Degree of Crystallinity /

Many reports have appeared on the synthesis of macromonomers using thiols such as 3-mercaptopropionic acid (3-MPA).^{1–3} Star-shaped polymers containing sulfur were prepared by radical polymerizations of macromonomers, and properties for paints were studied.^{4,5} Mercapto-modified polymers were highly adsorptive toward heavy metal ions⁶ and useful for chain transfer agents of the radical polymerization to synthesize graft copolymers.⁷ The substituted allylic sulfides obtained from thiols as chain transfer agents in the radical polymerization gave end-functional polymers of controlled molecular weights.⁸ From this point of view, thiols such as 3-MPA are very often utilized for polymerization retarders and regulators in the field of macromolecules.

The objective of our studies was to search for effective and wide applications of thiols such as 3-MPA, except for application in polymerization retarder and regulator. We previously reported the synthesis and characterization of the polymers containing sulfur in the main and side chain using 3-MPA.^{9,10}

This paper describes the synthesis and polymerization of novel monomers, 2-hydroxyethoxycarbonylethyl methoxycarbonylethyl sulfide (HEMS), 2-hydroxyethoxycarbonyl (2'-methyl) ethyl methoxycarbonylethyl sulfide (HMMS) and 3,3'-dithiodiethylcarboxy allyl (DTCA), which have a sulfide or disulfide group. Characterizations of the polymers were made by thermal and X-ray diffraction analyses, and NMR spectra.

EXPERIMENTAL

Materials

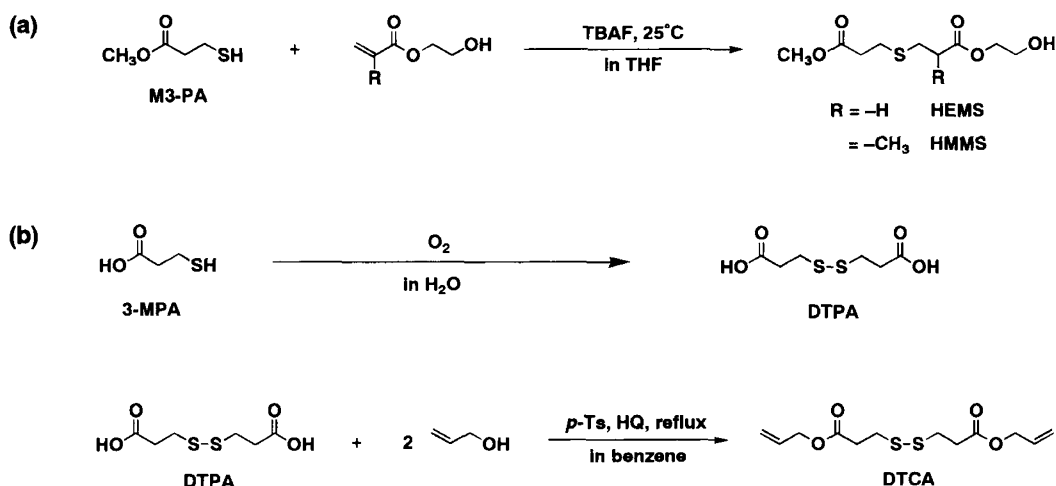
3-MPA and methyl 3-mercaptopropionate (M3-MP) were supplied by Nippon Oil & Fats Co., Ltd. 3-MPA, M3-MP, 2-hydroxyethyl acrylate (HEA), and 2-hydroxyethyl methacrylate (HEMA) were used after distilla-

tion under reduced pressure. Allyl alcohol, ethylene diamine (EDA), and hexamethylene diamine (HDA) were used after distillation. Tetrahydrofuran (THF) and toluene were dried over sodium metal and then used after distillation. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Other reagents were used without further purification. Monomers of HEMS, HMMS, and DTCA were synthesized, as drawn in Scheme 1.

HEMS. M3-MP (6.0 g, 5.0×10^{-2} mol) and an equimolar amount of HEA (5.8 g, 5.0×10^{-2} mol) were dissolved in THF (50 mL) in a Schlenk reaction tube. Tetrabutylammonium fluoride (TBAF) (5.0×10^{-4} mol) as catalyst was added to the solution, which was stirred at 25°C for 48 h under nitrogen atmosphere. The mixture was evaporated under reduced pressure and dissolved in suitable amount of ethyl acetate. The solution was washed with water and dried with anhydrous magnesium sulfate and filtered. The filtrate was evaporated under reduced pressure to give HEMS as a pale yellow oil. Further purification of HEMS was impossible because of the heat of oligomerization. HEMS may be used as a monomer, judging from ¹H and ¹³C NMR spectra: yield 55%; ¹H NMR [δ , ppm from tetramethylsilane (TMS) in CDCl₃] 4.27–4.24 (t, $J=4.62$, 2H, $-CH_2CH_2OH$), 3.85–3.82 (t, $J=4.62$, 2H, $-CH_2CH_2OH$), 3.71 (s, 3H, CH_3OCO-), 2.86–2.80 (m, 4H, $-CH_2CH_2SCH_2CH_2-$), 2.70–2.60 (m, 4H, $-CH_2CH_2SCH_2CH_2-$), 2.39 (b, 1H, $-OH$); ¹³C NMR (δ , ppm from TMS in CDCl₃) 172.29 (C=O), 171.99 (C=O), 66.23 ($-CH_2CH_2OH$), 60.97 ($-CH_2CH_2OH$), 51.83 (CH_3OCO-), 34.59 ($CH_3OCOCH_2CH_2S-$), 34.50 ($-SCH_2CH_2COOCH_2-$), 27.10 ($CH_3OCOCH_2CH_2S-$), 26.92 ($-SCH_2CH_2COOCH_2-$).

HMMS. HMMS is a pale yellow oil that was synthesized from M3-MP and HEMA by the same procedure as the synthesis of HEMS: yield 73%; ¹H NMR (δ , ppm from TMS in CDCl₃) 4.28–4.10 (m, 2H, $-CH_2CH_2OH$), 3.77–3.75 (t, $J=3.63$, 2H, $-CH_2CH_2OH$), 3.63 (s, 3H,

[†]To whom all correspondence should be addressed.



Scheme 1.

$\text{CH}_3\text{OCO}-$), 2.77–2.52 (m, 7H, $-\text{CH}_2\text{CH}_2\text{SCH}(\text{CH}_3)\text{CH}_2-$), 2.33 (b, 1H, $-\text{OH}$), 1.21–1.19 (d, $J=6.60$, 3H, $-\text{SCH}(\text{CH}_3)\text{CH}_2-$); ^{13}C NMR (δ , ppm from TMS in CDCl_3) 172.29 (C=O), 66.24 ($-\text{CH}_2\text{CH}_2\text{OH}$), 60.99 ($-\text{CH}_2\text{CH}_2\text{OH}$), 51.81 ($\text{CH}_3\text{OCO}-$), 40.11 ($-\text{SCH}(\text{CH}_3)\text{CH}_2-$), 35.64 ($-\text{SCH}(\text{CH}_3)\text{CH}_2-$), 34.58 ($-\text{OCOCH}_2\text{CH}_2\text{S}-$), 27.37 ($-\text{OCOCH}_2\text{CH}_2\text{S}-$), 16.84 ($-\text{SCH}(\text{CH}_3)\text{CH}_2-$).

3,3'-Dithiodipropionic Acid (DTPA). 3-MPA (2.2 g, 2.0×10^{-2} mol) was dissolved in distilled water (40 mL). The solution was stirred at 25°C for 72 h bubbling oxygen and filtered. The obtained product was washed with water and dried under vacuum to give DTPA as a white powder: yield 63%; mp 156–158°C; ^1H NMR (δ , in dimethyl sulfoxide ($\text{DMSO}-d_6$)) 12.37 (brs, 2H, $-\text{COOH}$), 2.93–2.88 (t, $J=6.93$, 4H, $-\text{CH}_2\text{CH}_2\text{S}-$), 2.67–2.62 (t, $J=6.93$, 4H, $-\text{CH}_2\text{CH}_2\text{S}-$); ^{13}C NMR (δ , in $\text{DMSO}-d_6$) 172.63 (C=O), 33.57 ($-\text{CH}_2\text{CH}_2\text{S}-$), 33.03 ($-\text{CH}_2\text{CH}_2\text{S}-$).

DTCA. DTPA (5.0 g, 2.4×10^{-2} mol), allyl alcohol (3.7 g, 6.4×10^{-2} mol), *p*-toluenesulfonic acid (0.1 g) and hydroquinone (0.1 g) were placed in benzene (100 mL). The solution was heated under reflux for 6 h, cooled to room temperature and then washed with water. The solution was dried with anhydrous magnesium sulfate and evaporated under reduced pressure to give DTCA as a colorless oil: yield 90%; ^1H NMR (δ , ppm from TMS in CDCl_3) 6.00–5.85 (m, 2H, $\text{CH}_2=\text{CH}-$), 5.37–5.22 (m, 4H, $\text{CH}_2=\text{CH}-$), 4.62–4.59 (m, 4H, $-\text{CH}_2\text{OCO}-$), 2.97–2.91 (m, 4H, $-\text{CH}_2\text{CH}_2\text{S}-$), 2.80–2.74 (m, 4H, $-\text{CH}_2\text{CH}_2\text{S}-$); ^{13}C NMR (δ , ppm from TMS in CDCl_3) 171.28 (C=O), 131.91 ($\text{CH}_2=\text{CH}-$), 118.49 ($\text{CH}_2=\text{CH}-$), 65.45 ($-\text{CH}_2\text{OCO}-$), 34.02 ($-\text{CH}_2\text{CH}_2\text{S}-$), 33.05 ($-\text{CH}_2\text{CH}_2\text{S}-$).

Polycondensations of HEMS and HMMS

HEMS (or HMMS) and metal acetate were placed in a round-bottomed flask fitted with a magnetic stirrer. Polycondensations were performed in three steps: the mixture was heated 180°C for 3 h, the system was subjected to reduced pressure of approximately 30 mmHg for 3 h, and then vacuum of approximately 0.1 mmHg for 3 h. After cooling to room temperature, the polymer was dissolved in CHCl_3 . The polymer solution was washed with water, evaporated under reduced pressure, and precipitated by an addition of methanol. The obtained

polymer was purified by reprecipitating it twice from the CHCl_3 solution to excess methanol. The polymer was decanted and dried under vacuum for 3 days.

Radical Polymerization of DTCA

Radical polymerizations were performed with AIBN and di-*t*-butylperoxide (DTBP) as initiator in a sealed tube at 60°C and 110°C under nitrogen atmosphere. After polymerization, the polymer solution was poured into a large amount of methanol to precipitate the polymer. The polymer was purified by reprecipitating it twice from the THF solution to excess methanol. The polymer was decanted and dried under vacuum for 3 days.

Polymerizations of DTCA with Diamine

Polymerizations of DTCA with EDA (or HDA) were carried out in a sealed tube or three-neck flask fitted with a magnetic stirrer at 60°C and 120°C under nitrogen atmosphere. After polymerization, the mixture was poured into excess methanol to precipitate the polymer. The polymer was decanted and dried under vacuum for 3 days.

Measurements

NMR spectra were recorded at 25°C using JEOL EX-270 (Jeol Ltd.). Gel permeation chromatography (GPC) measurements were carried out at 50°C on a Shimadzu SPD-10A (Shimadzu Ltd.) equipped with a UV detector and HSG-40, HSG-20, HSG-15, and HSG-10 columns using THF as an eluent. Thermal stability was measured by a differential scanning calorimeter with a SSC/5200 (Seiko Ltd.) and Shimadzu DSC-50. X-Ray diffraction analysis was carried out with a Shimadzu XD-D1.

RESULTS AND DISCUSSION

Polycondensations of HEMS and HMMS

The results of the polycondensations of HEMS and HMMS are summarized in Table I. Polycondensations were performed in the presence of several metal acetates used in previous work,⁹ and proceeded heterogeneously throughout. The resulting polymers were pale yellow rubbery and soluble in ordinary polar solvents such as

Table I. Polycondensation of HEMS and HMMS^a

Run	monomer	Catalyst mol%	Reaction temp °C	Reaction time/h			Yield ^b %	Content of type I ^c mol%	M_n^c $\times 10^{-3}$	M_n^d $\times 10^{-3}$	M_w/M_n^d	T_d^e °C	T_g^f °C
				760 mmHg	30 mmHg	0.02 mmHg							
1	HEMS	None	180	3	3	3	0(81) ^j	(62) ^j	(0.63) ^j	(1.35) ^j	— ^k	— ^k	
2	HEMS	AcONa(5)	180	3	3	3	71	— ^k	5.26	1.50	— ^k	— ^k	
3	HEMS	AcONa(10)	180	3	3	3	57(22) ^j	— ^k	4.28(1.23) ^j	1.21(1.30) ^j	— ^k	— ^k	
4	HEMS	AcONa(20)	180	3	3	3	66	82	6.39	1.89	206	-39.3	
5	HEMS	AcONa(50)	180	3	3	3	65	100	3.32	5.61	2.12	202	-39.6
6	HEMS	AcONa(80)	180	3	3	3	64	100	4.01	6.40	2.64	207	-39.1
7	HEMS	AcONa(100)	180	3	3	3	63	90	5.08	1.75	205	-40.2	
8	HEMS	(AcO) ₂ Ca·H ₂ O(10)	180	3	3	3	14	5	3.52	1.04	210	-51.0	
9	HEMS	AcOK(20)	180	3	3	3	52	100	4.58	4.44	1.35	196	-48.3
10	HEMS	(AcO) ₂ Zn·2H ₂ O(10)	180	3	3	3	53	— ^k	3.64	10.3	206	-53.9	
11	HEMS	(AcO) ₂ Pb·3H ₂ O(10)	180	3	3	3	66	— ^k	3.76	1.08	208	-50.0	
12	HMMS	AcONa(20)	180	3	3	3	12	— ^k	— ^k	— ^k	233	-44.4	
13	HMMS	AcONa(50)	180–230	6 ^g	3	2.5 ^h	21	— ^k	— ^k	— ^k	247	-39.6	
14	HMMS	(AcO) ₂ Ca·H ₂ O(5)	180	3	3	3	5	14	— ^k	— ^k	— ^k	— ^k	
15	HMMS	(AcO) ₂ Ca·H ₂ O(10)	180–230	6 ^g	0	4 ⁱ	15	0	2.34	3.51	1.04	— ^k	— ^k
16	HMMS	AcOK(20)	180	3	3	3	26	100	4.60	4.71	1.29	250	-44.2
17	HMMS	(AcO) ₂ Zn·2H ₂ O(10)	180	3	3	3	28	12	4.20	1.46	252	-48.3	
18	HMMS	(AcO) ₂ Pb·3H ₂ O(10)	180	3	3	3	23	— ^k	3.76	1.10	— ^k	— ^k	

^a Conditions; monomer=10 mmol, in bulk. ^b Methanol-insoluble part. ^c By ¹H NMR. ^d By GPC with polystyrene standards. ^e T_d , decomposition temperature by TG. ^f T_g , glass transition temperature by DSC. ^g Under nitrogen at 180°C. ^h 1 h at 180°C and 1.5 h at 230°C. ⁱ 1 h at 180°C and 3 h at 230°C. ^j Methanol-soluble and *n*-hexane-insoluble part. ^k Not determined.

chloroform and THF.

¹H NMR spectra of HMMS and poly(HMMS)s are shown in Figure 1. Some peaks assigned to methylene protons (Figures 1(1), 7, and 8) of HMMS at 4.28–4.10 ppm and 3.77–3.75 ppm sifted to one peak (Figures 1(2), 7, and 8) at 4.25 ppm after polycondensation. In Figure 1(3) a peak assigned to end methylene at 3.77–3.75 ppm was clearly observed but does not appear in Figure 1(2). These results suggest that the obtained polymers by the polycondensation of HRMS could have two structures (types I and II in Scheme 2). The use of AcONa and AcOK as catalysts gave more type I than type II polymer, but the use of (AcO)₂Ca·H₂O and (AcO)₂Zn·2H₂O gave more type II than type I polymer (Table I). It is difficult to clearly explain the reason, but the kinds of metals and hydrate moiety may play important roles. Especially poly(HMMS) (run 15) exhibited only type II, as shown in Figure 1(2), because of high polycondensation temperature at 230°C.

Yields of poly(HMMS) were lower than those of poly(HEMS) owing to steric hindrance α -methyl groups for HMMS. Figure 2 shows relationships between metal acetate amounts and yields, and M_n determined by GPC for poly(HEMS). AcONa and (AcO)₂Pb·3H₂O as catalysts gave the highest polymer yield. But with (AcO)₂Pb·3H₂O as catalyst, byproducts such as PbS were formed in the polycondensation of compounds having a sulfide such as 3-hydroxypropyl methoxycarbonyl ethyl sulfide (HPMES).⁹ Amounts of metal acetate scarcely influenced yields of methanol-insoluble polymers though the absence of metal acetate gave no methanol-insoluble polymers but *n*-hexane-insoluble oligomers (run 1; $M_n = 6.3 \times 10^2$, $M_w/M_n = 1.3$). The polycondensations of HPMES also could not proceed without metal acetate.⁹

M_n of poly(HEMS) obtained with AcONa exhibited relatively high value and was little influenced by the amount of catalyst, and M_w/M_n was nearly 2. M_w/M_n of polymers obtained by polycondensation is nearly 2.¹¹ With (AcO)₂Ca·H₂O, (AcO)₂Zn·2H₂O and (AcO)₂Pb·

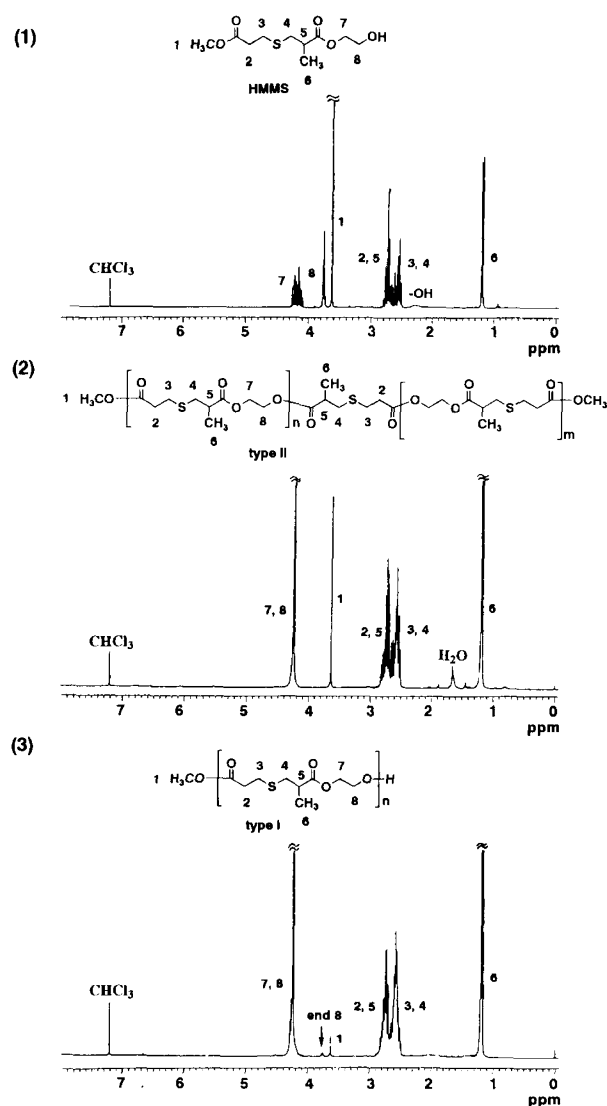


Figure 1. ¹H NMR spectra for HMMS and poly(HMMS) in CDCl₃ at 23.5°C (270 MHz); (1) HMMS, (2) run 15, and (3) run 16 in Table I.

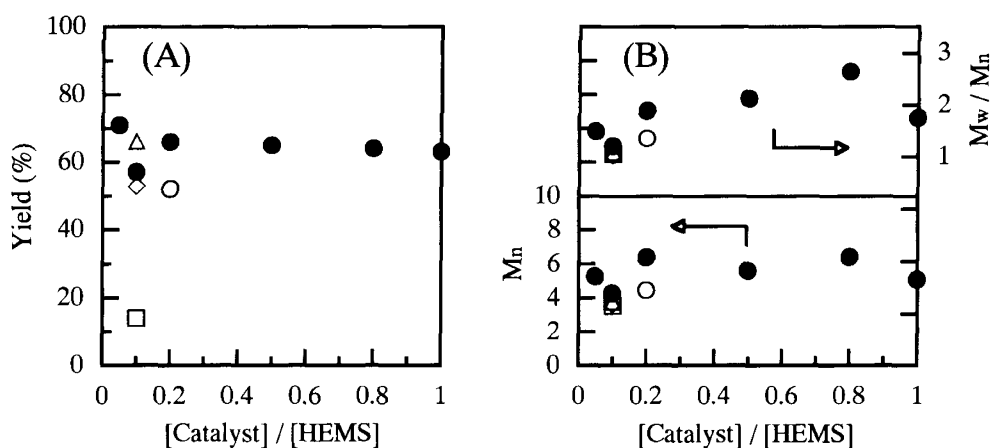
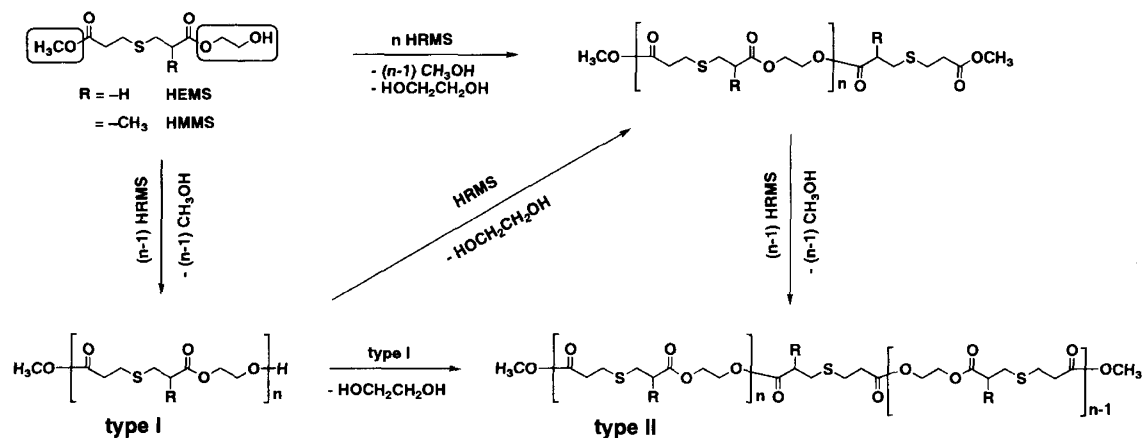


Figure 2. Relationships between amount of catalyst and (A) yield (%), and (B) M_n of poly(HEMS); (●) AcONa, (○) AcOK, (□) (AcO)₂Ca·H₂O, (◇) (AcO)₂Zn·2H₂O, and (△) (AcO)₂Pb·3H₂O.

Table II. Radical polymerization of DTCA

Run	DTCA mmol	Initiator ^a mol%	Solvent mL	Polym. temp °C	Polym. time h	Yield ^b %	M_n^c × 10 ⁻³	M_w/M_n^c
1	1.7	AIBN(1)	THF(1)	60	24	Trace		
2	1.7	AIBN(5)	THF(1)	60	24	Trace		
3	1.7	AIBN(10)	THF(1)	60	24	Trace		
4	1.7	DTBP(5)	None	110	24	4.1	2.3	1.67
5	1.7	DTBP(10)	None	110	24	8.7	2.7	1.46

^a AIBN, 2, 2'-azobisisobutyronitrile; DTBP, di-*t*-butylperoxide. ^b Methanol-insoluble part. ^c By GPC with polystyrene standards.

3H₂O as catalyst, M_n of poly(HEMS) was about 3.5×10^3 and M_w/M_n was nearly 1. The polymer having M_n lower than about 3500 may thus be soluble in methanol of precipitant. In fact, we recovered the methanol-soluble part whose M_n and M_w/M_n were 1.2×10^3 and 1.3, respectively (run 3).

Radical Polymerization of DTCA

The results of the radical polymerization of DTCA are summarized in Table II. The polymerization could not proceed with AIBN at 60°C, but with DTBP at 110°C to give the polymer of a pale yellow oil. Yields and M_n of the polymers were 4–9% and 2.3×10^3 – 2.7×10^3 , respectively, because of chain transfer by active hydrogen

of allyl groups.

¹H NMR spectra of DTCA and poly(DTCA) are shown in Figure 3. The peaks assigned to the main chain at 1.05–2.70 ppm and allyl group at 5.23–5.99 ppm were clearly observed. The ratio of the integrated intensity of peaks assigned to methine proton at 5.85–6.00 ppm and two ethylene groups neighboring a disulfide group at 2.75–2.97 ppm was 1 : 8. Thus poly(DTCA) may have allyl groups in the side chain end without crosslinkage.

Polyaddition of DTCA with Diamine

The results of the polymerizations of DTCA with EDA and HDA are summarized in Table III. Polymerizations

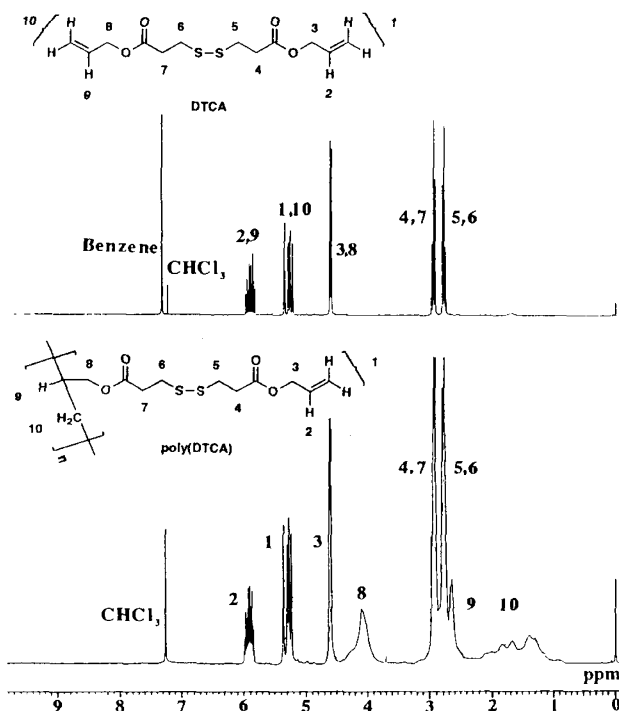


Figure 3. ^1H NMR spectra for DTCA and poly(DTCA) (run 5 in Table II) in CDCl_3 at 23.5°C (270 MHz).

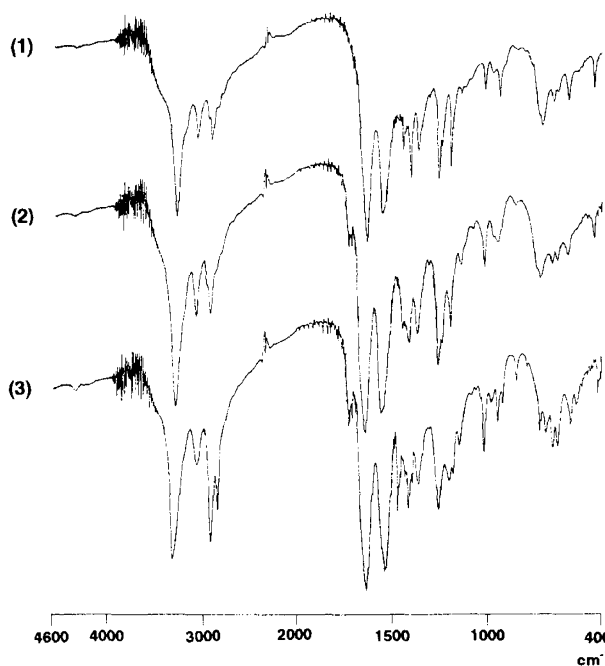


Figure 4. Infrared spectra for poly(DTCA-EDA) and poly(DTCA-HDA); (1) run 3, (2) run 4, and (3) run 6 in Table III.

were carried out in toluene and bulk at 60°C and 120°C to obtain the corresponding polymers of a pale yellow powder. The bulk polymerization without a catalyst gave the highest yield (run 5, 6). All the polymers were insoluble in general organic solvents such as acetone, benzene, methanol, chloroform, THF, DMF, and DMSO but only soluble in trifluoroacetic acid.

Figure 4 shows infrared spectra of the poly(DTCA-

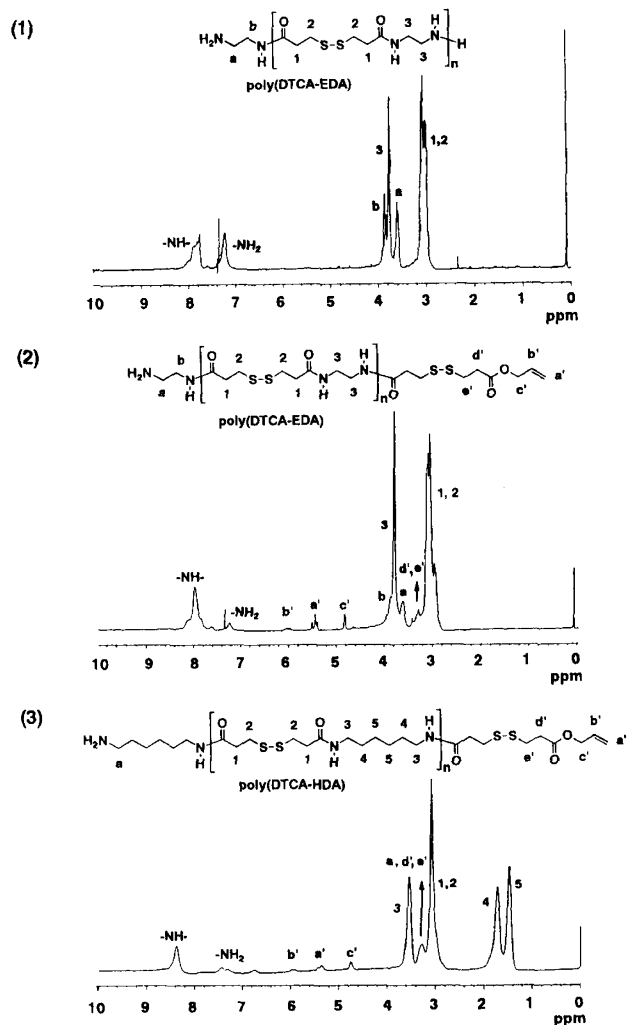


Figure 5. ^1H NMR spectra for poly(DTCA-EDA) and poly(DTCA-HDA) in trifluoroacetic acid/ CDCl_3 ($6/4_{\text{volume}}$) at 23.5°C (270 MHz); (1) run 3, (2) run 4, and (3) run 6 in Table III.

EDA) and poly(DTCA-HDA). Strong absorption due to amide groups was clearly observed at 1640 cm^{-1} and 1550 cm^{-1} for all the polymers. Absorption due to ester groups at 1720 cm^{-1} was very weakly or not observed. From these results the poly(DTCA-EDA) and poly(DTCA-HDA) may have linear structures by the condensation of DTCA with EDA and HDA, as shown in Figure 5. Insolubility of the polymers in several solvents could be attributed to the rigid amide groups. M_n s of the poly(DTCA-RDA)s determined by ^1H NMR spectra were $6.0 \times 10^2 - 2.1 \times 10^3$.

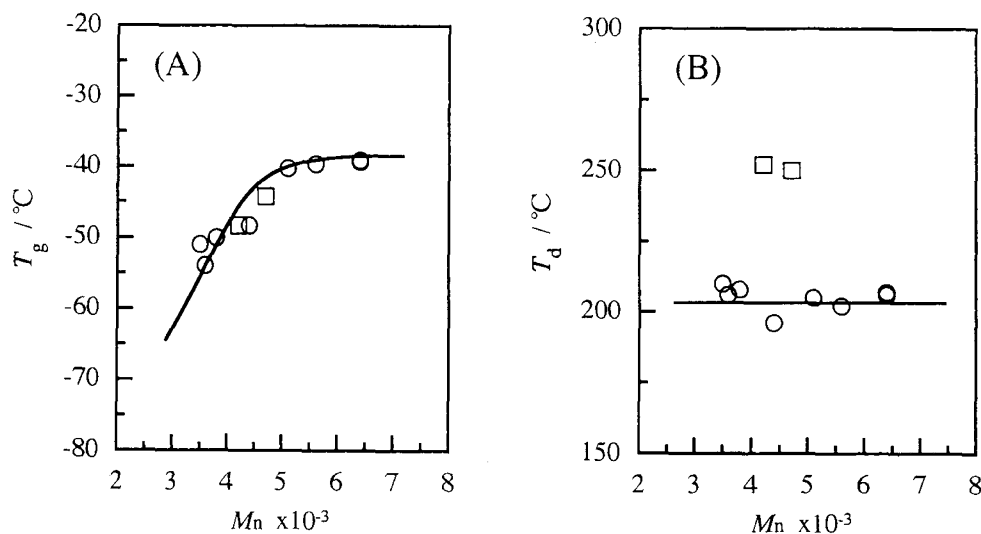
Characterization

Glass transition temperatures (T_g) and decomposition temperatures (T_d) of poly(HRMS)s were $-39 - -54^\circ\text{C}$ and $196 - 252^\circ\text{C}$, respectively, as shown in Table I. The low T_g is attributed to the sulfur atom in the main chain. Figure 6 exhibits relationships between M_n and T_g , and T_d of poly(HRMS)s. The T_g of the poly(HRMS)s increased with the M_n under 5.0×10^3 but T_d of the poly(HRMS)s did not depend on the M_n . T_g of poly(HMMS) was similar to that of poly(HEMS) but T_d of poly(HMMS) was higher than that of poly(HEMS). T_g is thus affected by α -methyl group but T_d could not be affected.

Table III. Polymerization of DTCA with Diamine^a

Run	Diamine	Catalyst ^b mol%	Polym. solvent ^c mL	Polym. temp °C	Polym. time h	Yield ^d %	M_n^e $\times 10^{-3}$	T_d^f °C	T_g^g °C	X ^h %
1	EDA	None	Tol.(25)	120	9	Trace				
2	EDA	EtONa(20)	Tol.(10)	120	24	Trace				
3	EDA	AIBN(10)	Tol.(1)	60	24	32.3	0.60	146	-1.0	49.3
4	EDA	DTBP(10)	None	120	1	31.7	2.11	146	-4.7	28.7
5	EDA	None	None	60	30	49.7	— ⁱ	— ⁱ	— ⁱ	— ⁱ
6	HDA	None	None	60	30	50.9	1.85	182	-3.2	25.0
7	HDA	AIBN(10)	Tol.(1)	60	30	27.2	1.65	178	-1.0	26.7
8	HDA	None	Tol.(1)	60	30	26.6	— ⁱ	176	— ⁱ	27.1

^a DTCA = 1.8 mmol; diamine = 1.8 mmol; EDA, ethylenediamine; HDA, hexamethylenediamine. ^b EtONa, sodium ethoxide; AIBN, 2,2'-azobisisobutyronitrile; DTBP, di-*t*-butylperoxide. ^c Tol., Toluene. ^d Methanol-insoluble part. ^e By ¹H NMR. ^f T_d , decomposition temperature by TG. ^g T_g , glass transition temperature by DSC. ^h X, crystallinity by XRD. ⁱ Not determined.

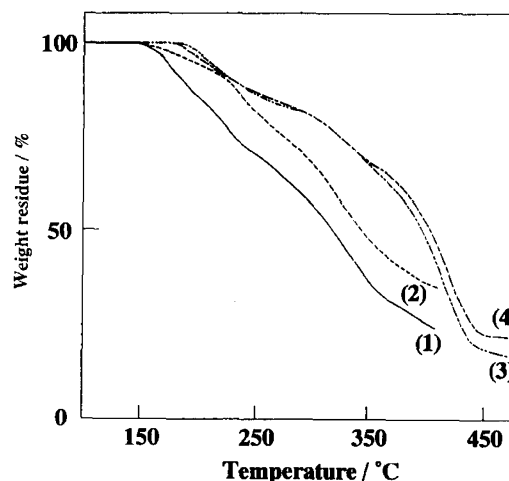
**Figure 6.** Relationships between M_n and (A) T_g and (B) T_d for (○) poly(HEMS) and (□) poly(HMMS).

T_g and T_d of the poly(DTCA-EDA)s and poly(DTCA-HDA)s were -4.7 — -1.0 °C and 146 — 182 °C, respectively, as shown in Table III. Figure 7 shows typical TG curves of the polymers. TG curves of poly(DTCA-HDA)s (runs 6 and 7 in Table III) exhibited similar tendency. However poly(DTCA-EDA)s (runs 3 and 4 in Table III) showed different TG curves.

Figure 8 depicts typical X-ray diffraction diagrams of poly(DTCA-EDA)s and poly(DTCA-HDA)s. The results indicate that the polymers are in amorphous and crystal states. Crystallinity was determined from area of crystalline and amorphous region in X-ray diffraction diagrams, as shown in Table III. And that of poly(DTCA-HDA)s (runs 6 and 7 in Table III) was similar, 25.0% and 26.7%, but different for poly(DTCA-EDA)s (runs 3 and 4 in Table III), 49.3% and 28.7%, respectively. It is difficult to clearly explain the reason, but these results may be attributed to different molecular weights and/or structures of polymer end groups (Table III and Figure 5).

CONCLUSION

Three new monomers containing sulfur, HEMS, HMMS, and DTCA were synthesized from 3-MPA. The polycondensations of HEMS and HMMS were carried

**Figure 7.** Typical TG curves of poly(DTCA-EDA) and poly(DTCA-HDA); (1) run 3, (2) run 4, (3) run 6, and (4) run 7 in Table III.

out with several metal acetates as catalysts to obtain the corresponding polythioethers with M_n of up to 6.4×10^3 , T_g of -39 — -54 °C and T_d of 196 — 252 °C. The radical polymerizations of DTCA were performed in bulk at 110 °C to form polymers having allyl groups in the side chain

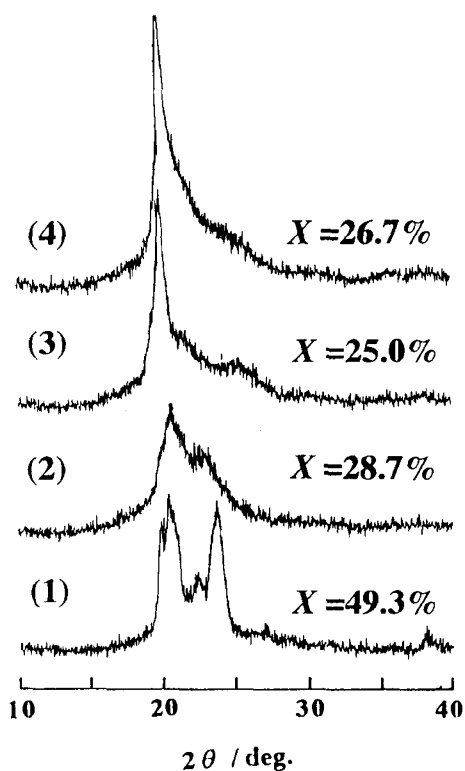


Figure 8. Typical XRD diagrams of poly(DTCA-EDA) and poly(DTCA-HDA); (1) run 3, (2) run 4, (3) run 6, and (4) run 7 in Table III.

with M_n of up to 2.7×10^3 . The polycondensations of DTCA with EDA and HDA were accomplished to obtain the corresponding polymers with T_g of -5 — -1°C , T_d of 146 — 182°C and crystallinity of 25 — 49% .

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