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CYCLOPOLYMERIZATION OF DIALLYL MALONONITRILE AND THE THIOETHER DIMER OF ETHYL α-CHLOROMETHYLACRYLATE

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ABSTRACT

Two new monomers for cyclopolymerization were synthesized and polymerized in good yield to the corresponding polymers. A dicyano-containing diallyl species was obtained through a phase-transfer catalyzed reaction between diallyl chloride and malononitrile. The diallyl malononitrile (DAM) thus obtained underwent AIBN-initiated thermal polymerization in bulk at 80°C to give a low molecular weight, soluble cyclopolymer with a glass transition temperature of 123°C. Solution ^{1}H- and ^{13}C-NMR spectra for the cyclopolymer suggest high cyclization efficiency and exclusive five-membered ring formation with *cis*-dominated configurations of the recurring cyclopentane ring. Investigation of the copolymerization of DAM and methyl acrylate shows that cyclization efficiency of the diallyl malononitrile units decreased with an increase in methyl acrylate concentration. Kinetic evaluation of the copolymerization gave values of $k_C/k_{ID} = 68$ mol/L and $k_C/k_{IM} = 17$ mol/L where the subscripts "C," "ID," and "IM" indicate intramolecular cyclization, intermolecular addition of diallyl malononitrile, and intermolecular addition of methyl acrylate, respectively. These values imply that the high cyclization efficiency of DAM is lowered by copolymerization with methyl acrylate owing to more rapid cross-propagation of the uncyclized radical to methyl acrylate than to diallyl malononitrile ($k_{IM}/k_{ID} = 4$); i.e., a slower intermolecular reaction allows more time for intramolecular cyclization. The thioether diacrylate monomer was obtained directly from the reaction of sodium sulfide and ethyl α-chloromethylacrylate in yields of ~70%. Solution polymerization was unsuccessful, but bulk polymerization with AIBN gave good conversion to soluble cyclopolymer of low viscosity and molecular weight (~3,000 by SEC). ^{1}H- and ^{13}C-solution NMR indicated that the polymer contains 6-membered rings in the repeat units along with <5% residual unsaturation due to end-groups or noncyclized repeat units. Both of these systems are surprising in that *any* soluble cyclopolymer was obtained given the low reactivity displayed by nonstabilized allyl monomers and the high degree of degradative chain transfer expected for the thioether moiety.

INTRODUCTION

It is well known that the polymerization of many 1,6-heptadienes proceeds through sequential intramolecular-intermolecular propagation to give soluble cyclopolymers under appropriate conditions [1]. We have been investigating radical cyclopolymerization of some symmetrical diacrylates [2–4] which give novel cyclopolymers containing six-membered ring repeat units in the polymer backbone. Especially interesting is the diacrylate-containing malononitrile group as the central connecting unit, which shows complete cyclization and high stereoregularity in the cyclopolymerization step [3]. Incorporation of malononitrile groups into polymer backbones or side-chains has potential for generating piezo- and pyroelectric materials due to large inherent dipole moments; the dicyano groups of poly(vinylidene cyanide) copolymers generate excellent piezoelectric behavior [5].

Although allyl compounds generally show sluggish polymerizability, diallylammonium salts give soluble high-molecular weight polymers with efficient cyclopolymerization due to polarization of the allyl vinyl bond [1]. Most neutral diallyl monomers give only very low molecular weight polymers with a low degree of cyclization. Attempts have been made to quantitate radical polymerizability of allyl monomers [6, 7]. It was reported that reaction media which increased the electron-withdrawing ability of the allyl substituent (e.g., strong acid) decreased degradative chain transfer and increased polymerizability [6]. We earlier proposed the application of both ^{13}C-NMR spectroscopy and MINDO/3 calculations for prediction of polymerizability of mono- and diallyl monomers, and found good correlation between electron density (calculated or measured by chemical shift) and ease of polymerization [7].

We decided to investigate synthesis and cyclopolymerization of diallyl malononitrile with the expectation that the strong electron-withdrawing ability of the dicyano group would enhance the polymerizability and cyclization efficiency of the allyl moieties. We also briefly investigated copolymerization of DAM with methyl acrylate in order to quantitate the comonomer effect on the cyclization efficiency of this new monomer. Finally, study of the thioether dimer was intended as a worst-case example for evaluating the role of the radical stabilizing group (in this case the acrylate ester) on the relative ease of cyclopolymerization versus degradative chain transfer.

EXPERIMENTAL

Malononitrile, allyl chloride, sodium sulfide, and tetrabutylammonium bromide (TBAB) were purchased from Aldrich Chemical Company and used as obtained. 2,2′-Azobis(isobutylonitrile) (AIBN) was recrystallized from methanol before use. ^{1}H- and ^{13}C-NMR spectra were obtained on Bruker AC-200 and AC-300 spectrometers. Thermal transitions were measured on a Du Pont 9900 thermal analyzer using a model 910 DSC cell at a heating rate of 10°C/min under nitrogen flow. Size-exclusion chromatography (SEC) was performed on American Laboratory columns using THF solvent, polystyrene standards, and a differential refractometer detector.

Synthesis of 2,2-Diallylmalononitrile (DAM)

Diallyl malononitrile (DAM) was synthesized according to the following procedure involving phase-transfer catalysis. To a stirring mixture of allyl chloride (24.4 g, 0.318 mol), malononitrile (10.0 g, 0.151 mol), TBAB (1.0 g, 3.1 mmol), and methylene chloride (100 g) was added a solution of KOH (20.6 g, 0.318 mol) in 100 mL water. The mixture was stirred at 0°C for 3 hours, and then at ambient temperature for 10 hours. The organic layer was separated, evaporated under reduced pressure, and distilled under vacuum to give pure DAM as white crystals; 31% yield; mp 32°C; ^{1}H NMR ($CDCl_3$): δ 5.95–58.1 (m, 1H), 5.43–5.36 (t, 2H), 2.67 (d, 2H); ^{13}C-NMR ($CDCl_3$): δ 128.7, 123.1, 114.9, 40.6, 37.3.

Typical Polymerization Conditions for DAM

To a 25-mL two-neck round-bottom flask equipped with a small magnetic stir-bar were added DAM, methyl acrylate (MA), and AIBN in the amounts indicated in Table 2. The mixture was subjected to nitrogen deaeration and placed in an oil bath preheated to 80°C. The resulting polymer was purified by reprecipitation twice into methyl alcohol or *n*-hexane. Polymerization conversions were determined from the product weight after purification. The fraction of uncyclized DAM units in the polymer was calculated from the relative intensity of residual double bond protons (5.1–6.0 ppm) in the ^{1}H-NMR spectrum. The fractions of methyl acrylate units in the copolymers were calculated from the relative intensities of the methyl protons (3.5–4.0 ppm) to backbone protons.

Synthesis of Thioether Diacrylate

Ethyl α-(chloromethyl)acrylate (ECMA) [3] (6.7 g, 0.045 mol), benzene (thiophene-free, 25 mL), sodium sulfide (5.1 g, 0.0653 mol), and a Teflon-coated magnetic stir-bar were added to a round-bottom flask. Dry nitrogen was used as purge gas. The mixture was stirred for 24 hours. Monitoring by GC was used to determine completion of reaction. Salts were removed by dissolution in water and separation of the organic phase. Evaporation of the solvent gave 96% pure sulfide dimer in 67% yield.

An alternative procedure involved reacting ethyl α-(chloromethyl)acrylate (3.1 g, 0.021 mol), sodium sulfide nonahydrate (2.5 g, 0.010), deionized water (2 mL), and a Teflon-coated magnetic stir-bar in a round-bottom flask under dry nitrogen for 24 hours. Ethyl ether (10 mL) and hexane (10 mL) were added, the organic phase separated, and solvents evaporated to give 89% pure sulfide dimer in 65% yield.

Thioether Diacrylate Polymerization

Bulk polymerization involved addition of 0.5 mol% AIBN to neat monomer, three freeze-evacuate-thaw cycles, and heating in a 60°C oil bath. Polymerization was considered complete when the monomer would not flow and nitrogen bubbles remained suspended in the solid. Typical polymerization times ranged from 24 hours to 6 days, and gave polymer in 50–75% yield. Solution polymerization in benzene failed to give substantial polymer, probably due to slow polymerization and side-reactions.

RESULTS AND DISCUSSION

Synthesis and Characterization of DAM

The overall synthesis and polymerization of DAM are given in Fig. 1. Slight excesses of allyl chloride and KOH to malononitrile were used to avoid residual monofunctional product in the reaction mixture. The reaction conversion to DAM was estimated to be 86% by GC, with no detectable malononitrile or monoallyl derivative. Lower yield of the purified sample (31%) was mainly due to loss during the distillation process. Displacement of the chlorine of allyl chloride was clean due to the occurrence of allylic attack although the reaction rate was lower than that for chloromethylacrylates with malononitrile [3]. ^{1}H- and ^{13}C-NMR spectra (the latter is given in Fig. 2) confirmed the structure of the product; no impurities were detected by GC or NMR, and we believe this synthesis could be carried out on a larger scale in essentially quantitative yield.

Table 1 shows chemical shift data for various allyl compounds abstracted from previous literature [7] in which the ^{13}C-NMR chemical shift differences ($\Delta\delta$) of the two vinyl carbon peaks were correlated with radical polymerizability. Comparison of the value for DAM ($\Delta\delta$ = 5.5 ppm) to those of other allyl compounds listed supports the expectation of fair-to-good polymerizability. That is, the strong

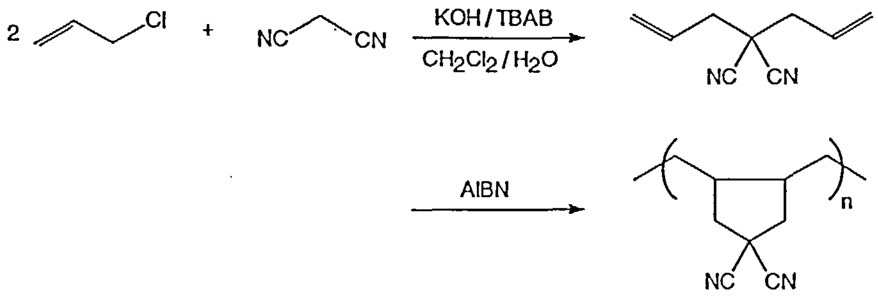

FIG. 1. Overall synthesis and cyclopolymerization of diallyl malononitrile.

TABLE 1. ^{13}C-NMR Chemical Shifts of Allyl Monomers (in $CDCl_3$)

Allyl monomer	Alkene chemical shifts (ppm)			
	$-CH=$	$=CH_2$	$\Delta\delta$	Polymerizability
N,*N*-Dimethyl-*N*,*N*-diallylammonium chloride	128.4	125.4	3.0	Good
N,*N*-Diallylamine hydrochloride	128.1	125.0	3.1	Good
4-(*N*,*N*-Diallylamino)pyridine hydrochloride	130.7	118.3	12.4	Poor
Allyl chloride	134.3	118.3	16.0	None
Allyl alcohol (conc HCl)	136.1	118.0	17.9	None
Diallylamine	136.7	117.6	19.1	None
Allyl alcohol	137.8	115.9	21.9	None
Diallyl malononitrile	128.7	123.1	5.5	Fair

electron-withdrawing effect of the dicyanomethylene group (which results in the small $\Delta\delta$ value in the ^{13}C-NMR spectrum) should also decrease degradative chain transfer by polarizing and strengthening the α-CH_2 bonds, consequently increasing polymerizability.

Synthesis and Characterization of Cyclopolymer

AIBN-initiated polymerization of DAM in bulk proceeded slowly but without crosslinking to give soluble cyclopolymers of low molecular weight. That is, despite the expectation of good polymerizability based on the ^{13}C NMR spectral comparison of DAM with other allyl monomers, propagation was slow compared to termination and transfer reactions. This is confirmed by the low conversions obtained even for extended reaction times. Table 2 shows the homopolymerization results together with those for copolymerization study with methyl acrylate.

The ^{13}C-NMR spectrum of DAM homopolymer is shown in Fig. 2 (Run 1, Table 2). Structural assignments was made using DEPT 135 and ^{13}C-^{1}H coupled experiments. DEPT results clearly showed the presence of two major methylene carbons: a sharp, strong peak at 17 ppm was assigned to backbone methylene carbons and the other broad peak at 42 ppm to ring methylene groups. Minor peaks around the major backbone methylene peak were attributed to methylene carbons of terminal DAM units. Since only one peak was seen in the region of the backbone methylene carbon, it was concluded that the cyclopolymer obtained has exclusively five-membered rings. This is in good agreement with the results reported for non-substituted 1,6-heptadienes in which kinetically preferred five-membered ring formation dominates over thermodynamically preferred six-membered ring generation [1]. A sharp peak seen at 38 ppm was attributed to ring quaternary carbons from the results of the ^{13}C-^{1}H coupled experiment in which no splitting was observed for this peak. Cyano carbons appeared as two peaks at 120 and 126 ppm with similar intensities. These peaks were attributed to two different cyano carbons of a *cis*-fused

TABLE 2. Results of Cyclohomo- and -copolymerization of Diallyl Malononitrile at 80°C

No.	Feed			Time	Conversion,[a] %	Polymer composition, mol%[b]			
						DAM			
	[DAM], mol/L	[MA], mol/L	AIBN, wt%			Cyclized	Open	MA	f_C
1	6.14	–	6.0	1 d	8	98.8	1.2	–	0.988
2	6.14	–	1.0	20 h	2	83.8	16.2	–	0.838
3	5.80	0.63	1.0	17 h	3	69.8	12.4	17.9	0.850
4	4.98	2.11	1.0	2.5 h	2	55.5	16.5	28.0	0.771
5	3.96	3.95	1.0	1.0 h	10	27.9	10.1	62.0	0.734
6	2.99	5.71	0.2	1.0 h	12	10.2	3.93	85.8	0.723
7	2.68	6.27	0.2	1.0 h	8	12.9	6.23	80.8	0.674
8	1.04	9.23	0.1	0.6 h	12	4.0	Trace	96.0	–

[a] Precipitant for polymer purification: methanol for Entry 1, *n*-hexane for Entries 2-8.
[b] Determined by ^{1}H NMR in DMSO-d_6 for Entries 1-4, $CDCl_3$ for Entries 5-8.

cyclopentane ring as shown in Fig. 2; one CN is shielded by the bulky polymer chain segments while the other is not. A similar peak pattern was observed for the cyano carbons of the cyclopolymers derived from dimethacryl malononitrile containing *cis*-dominated six-membered ring structures [3]. The larger chemical shift difference observed here (6 ppm) compared with that for the latter cyclopolymer (2.3 ppm) is attributable to the higher rigidity of five-membered rings. The predominance of *cis* addition may be explained by the hyperconjugation effects of the radical and adjacent alkyl C—H orbitals [1].

Three small sharp peaks seen at 25-31 ppm are attributed to the methyl (25.8 and 26.9 ppm) and quaternary (31.0 ppm) carbons of terminal AIBN residues. This was confirmed by benzoylperoxide-initiated cyclopolymerization which showed no peaks in this region. Number-average molecular weight of the cyclopolymer was estimated to be 1000-1500 from the intensity ratio of the methylene and methine protons in the ^{1}H-NMR spectrum of the cyclopolymer to the methyl protons seen at 1.3 ppm derived from terminal AIBN groups supposing one AIBN moiety per molecule. DSC analysis of the cyclopolymer showed a fairly high glass transition temperature of 123°C in spite of the apparent low molecular weight. In addition to the rigid and polar ring structure containing the malononitrile unit, the high stereoregularity described above may be responsible for the high T_g.

Copolymerization with Methyl Acrylate and Kinetic Consideration

The results of the copolymerization study are listed in Table 2 (Entries 2-8). *n*-Hexane was used as precipitant for purification of the copolymers to get accurate conversion data (a considerable portion of each polymer dissolved in methyl alcohol). The polymerization rate increased with an increase of methyl acrylate compo-

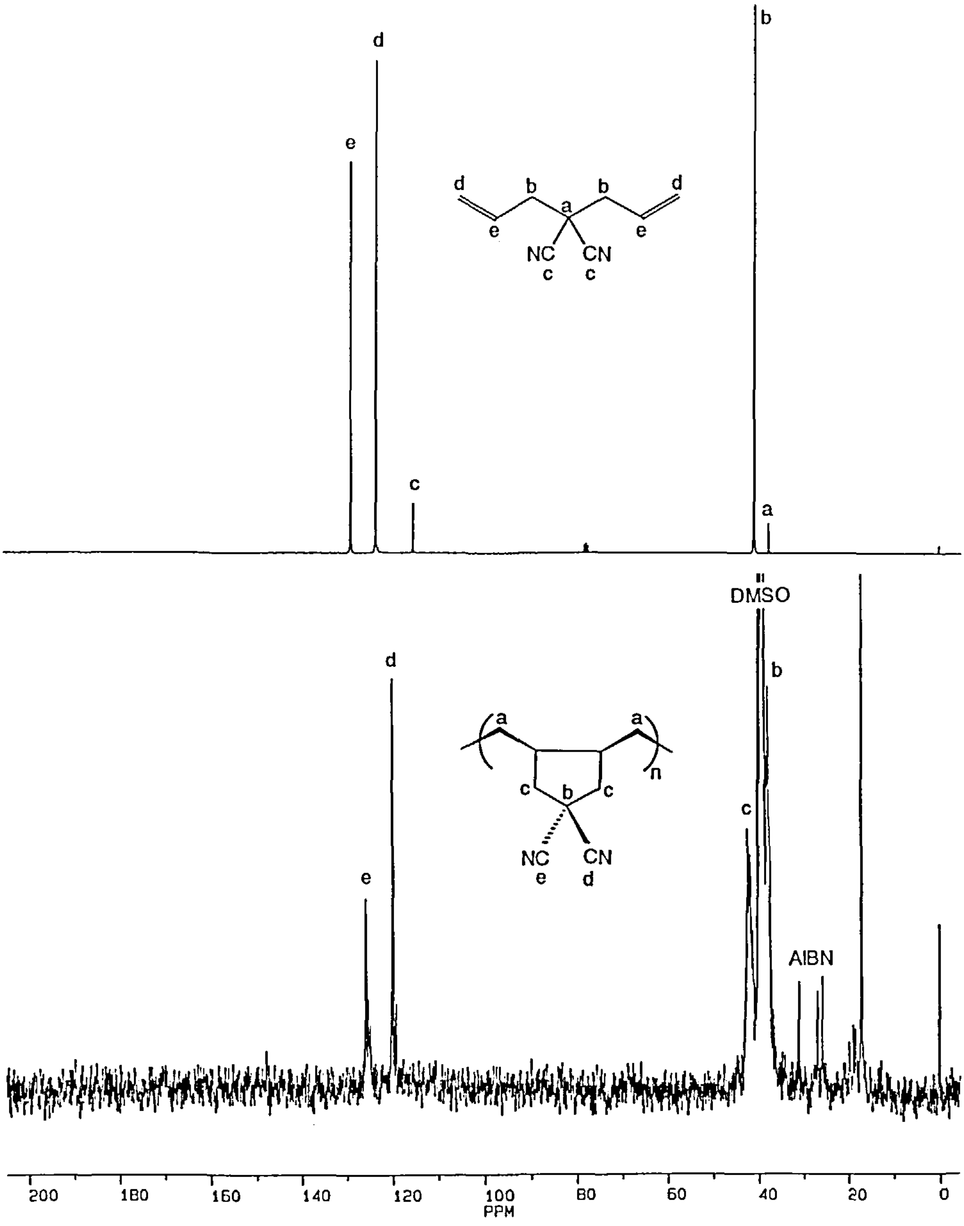

FIG. 2. ^{13}C-NMR spectra (CDCl$_3$) of diallyl malononitrile (upper trace) and its cyclopolymer (lower trace).

sition while the cyclization efficiency decreased as shown in Table 2. Figure 3 illustrates possible reactions of uncyclized cyclomonomer radical involving intramolecular cyclization (indicated by subscript "C"), intermolecular addition to cyclomonomer (indicated by "ID"), and intermolecular addition to monofunctional acrylate (indicated by "IM"). When polymerization conversion is kept low, the ratio of open cyclomonomer units (residual unsaturation in the cyclopolymer) to cyclized units is related to the three reaction rates described above as expressed by

$$(1 - f_C)/f_C = (R_{ID} + R_{IM})/R_C \tag{1}$$

where f_C symbolizes the fraction of cyclized units to all cyclomonomer units in the polymer formed. The reaction rates for the steps in Fig. 3 are expressed by

$$R_C = k_C[P^\bullet] \tag{2}$$

$$R_{ID} = 2k_{ID}[P^\bullet][D] \tag{3}$$

$$R_{IM} = k_{IM}[P^\bullet][M] \tag{4}$$

where $[P^\bullet]$, [D], and [M] symbolize concentrations of uncyclized radical, cyclomonomer, and comonomer, respectively. Equations (1)-(4) are combined to give the relationship

$$(1 - f_C)/f_C[D] = 2k_{ID}/k_C + k_{IM}[M]/k_C[D] \tag{5}$$

Therefore, a plot of $(1 - f_C)/f_C[D]$ versus [M]/[D] should give a straight line with an intercept of $2k_{ID}/k_C$ and a slope of k_{IM}/k_C. Using this plot, we can estimate the cyclization efficiency of the cyclomonomer and the effect of monofunctional comonomer on cyclization efficiency at the same time. Figure 4 shows this plot for

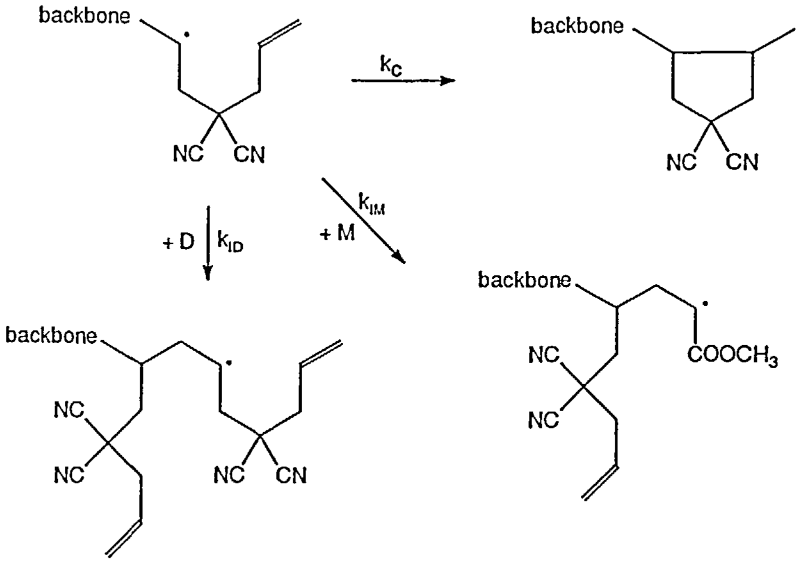

FIG. 3. Intramolecular cyclization and intermolecular addition of propagating radical with diallyl malononitrile and methyl acrylate.

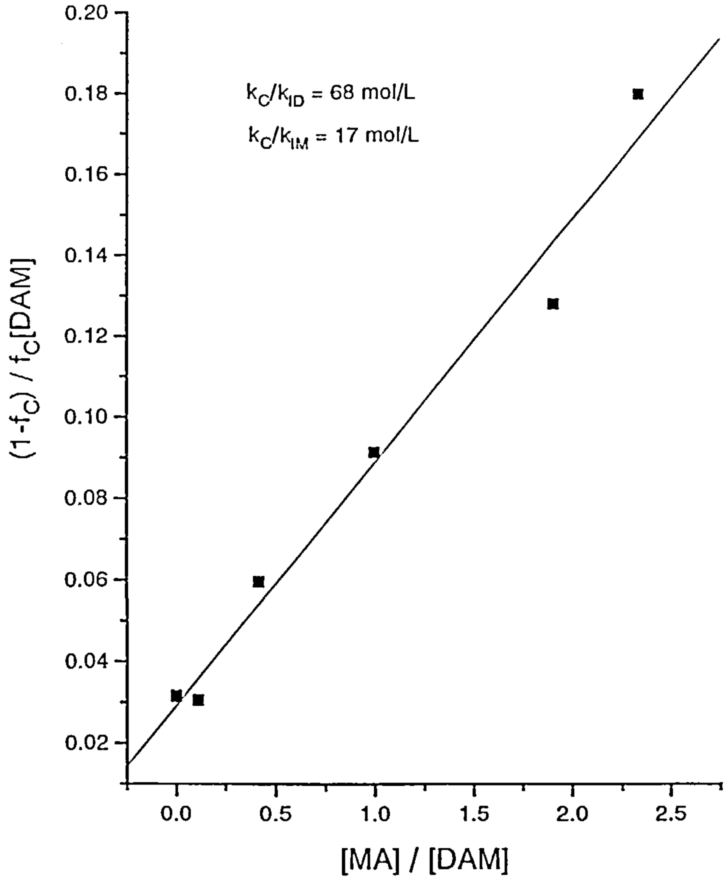

FIG. 4. Plot of [MA]/[DAM] versus $(1 - f_C)/f_C$[DAM].

the copolymerization of DAM and methyl acrylate. The linear relationship observed is in good agreement with the kinetic consideration given above. The ratios of reaction rates k_C/k_{ID} and k_C/k_{IM} were estimated to be 68 and 17 mol/L. These values imply that the high cyclization efficiency of DAM (k_C/k_{ID} = 68 mol/L) is lowered by copolymerization with methyl acrylate, probably owing to the more rapid cross-propagation of uncyclized radical with methyl acrylate (k_{IM}/k_{ID} = 4).

An attempt to determine the monomer reactivity ratios r_1 and r_2 (M_1: diallyl malononitrile; M_2: methyl acrylate) using the Fineman-Ross method was not successful, possibly due to the different reactivities between cyclized and uncyclized DAM radicals toward methyl acrylate. However, the value of r_2 appears to be larger than 1, which means that methyl acrylate is more reactive than diallyl malononitrile toward terminal methyl acrylate radical. This is reasonable given the lack of radical stabilization for the intermediate radical formed from the allyl moiety.

Synthesis and Cyclopolymerization of the Thioether Monomer

The ready nucleophilic displacement of the allyl chloride group of ECMA by various alcohols in the presence of base [3, 8, 9] prompted us to make the thioether

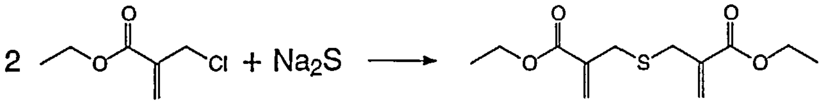

FIG. 5. Formation of the thioether diacrylate cyclomonomer.

diacrylate to see how far we could push the cyclopolymerizability of acrylate dimers containing moieties susceptible to radical fragmentation via degradative chain transfer. That is, would the thioether dimer undergo cyclopolymerization to polymer containing six-membered rings in the polymer backbone (as the ether analogs do) or would competitive chain transfer result in no polymerization or cyclization?

Synthesis of the monomer was extremely facile and occurred in high yield by direct reaction with sodium sulfide (Fig. 5). We were somewhat surprised that, as long as a 1:1 stoichiometry was maintained, subsequent Michael addition of the intermediate sulfide did not occur as was observed in the 1:1 reaction of ECMA with dithiols to give polythioethers [10]. Further reaction of the diacrylate in this manner is certainly feasible.

Radical polymerization of the diacrylate was possible in bulk but not in solution. Apparently, the concentration of acrylate groups must be kept high to facilitate addition to the radical chain end or competitive fragmentation becomes the favored process (Fig. 6). The latter gives a terminal acrylate group that has a sterically large substituent (R) attached at the α-CH_2 group. Based on the well-known nonpolymerizability of acrylates with α-alkyl substituents larger than methyl [11, 12], these terminal groups should not react like macromonomers to give pendant oligomer or polymer units. Overall, if this pathway was prevalent, no polymer would be obtained, and since polymer was obtained, propagation to give either cyclopolymer units or linear units (Fig. 7) is believed to be the major reaction pathway.

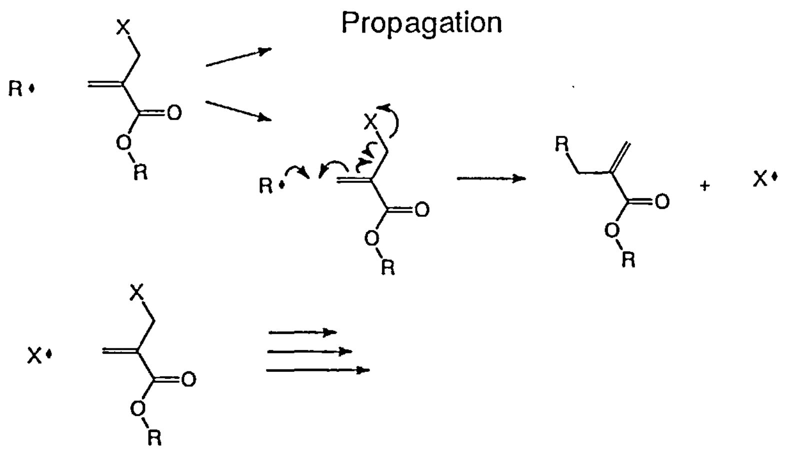

FIG. 6. Propagation and fragmentation reactions possible during free-radical reaction of the thioether diacrylate monomer.

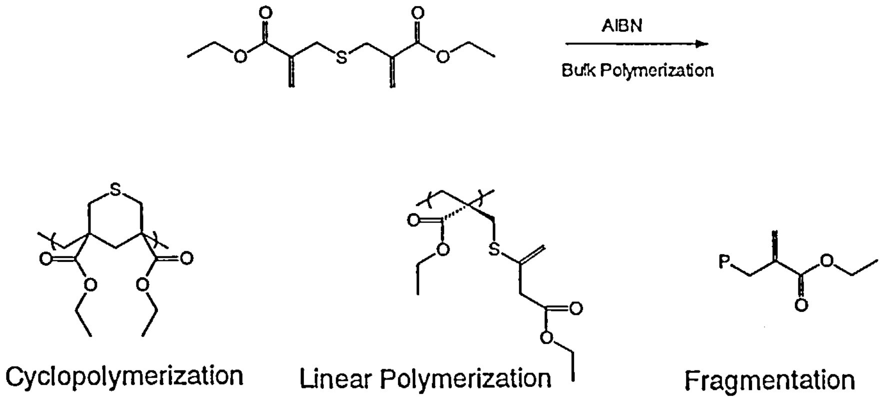

FIG. 7. Repeat unit structures and nonreactive fragmentation product from radical reactions of the thioether diacrylate.

Spectroscopic characterization of the polymer obtained clearly supports the conclusion that cyclopolymerization did take place. Figures 8 and 9 give the ^{13}C and ^{1}H solution NMR spectra of the thioether dimer and the polymer obtained from bulk polymerization with AIBN. The ^{13}C spectrum of the polymer is surprisingly clean, with no obvious end-groups or pendant vinyl units evident. The peak

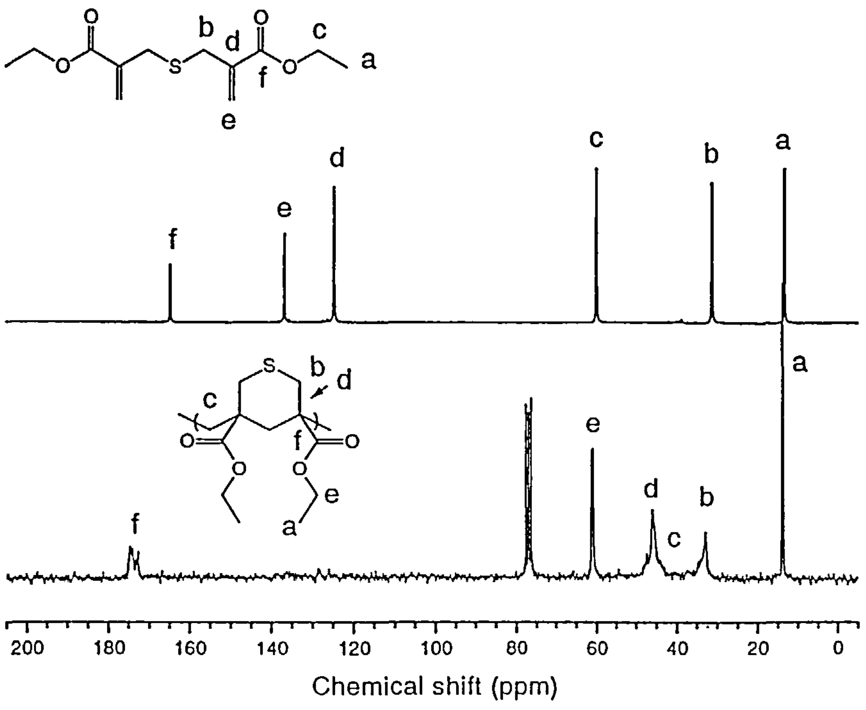

FIG. 8. ^{13}C-NMR spectra ($CDCl_3$) of the thioether dimer (upper trace) and its cyclopolymer (lower trace).

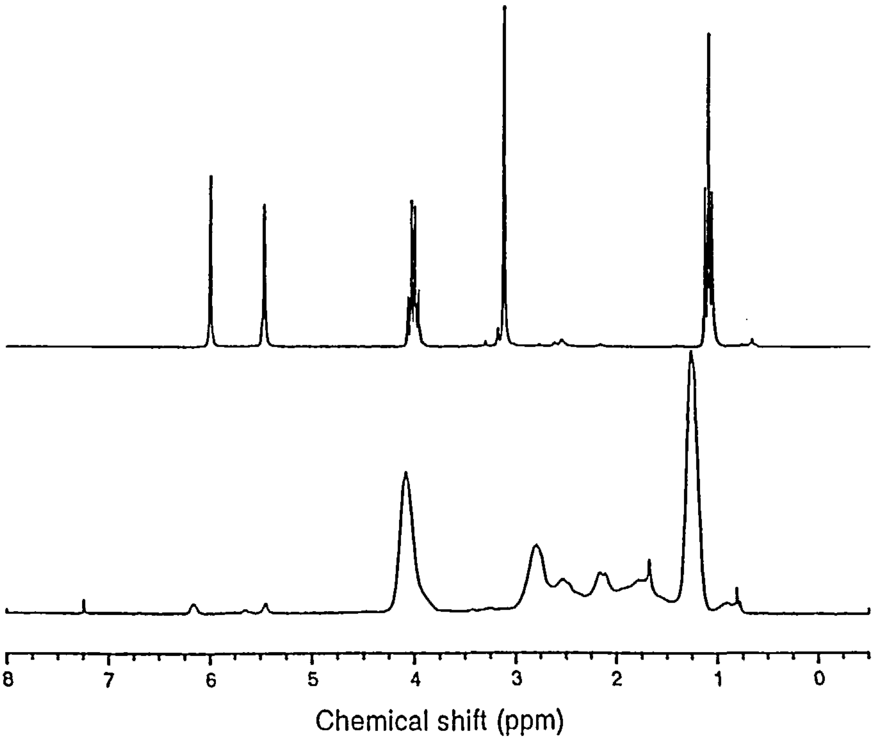

FIG. 9. ^{1}H-NMR spectra ($CDCl_3$) of the thioether dimer (upper trace) and its cyclopolymer (lower trace) with the latter showing residual double bond protons at ~5.3–6.2 ppm.

assignments given in the figure are consistent with DEPT experiments and previous analyses carried out in this laboratory on ether cyclopolymers. The ^{1}H-NMR spectrum of the polymer, however, does show residual alkene groups between 5.3 and 6.2 ppm; integration with respect to the remaining polymer peaks indicates a cyclization efficiency of >90%. What is unexpected here is not the relatively high degree of cyclization taking place, but the fact that *any* polymerization occurs in view of possible side reactions involving degradative and non-degradative chain transfer which would be expected to be very facile given the extensive literature precedence for related reactions.

CONCLUSIONS

These new monomers test the limits of free-radical cyclopolymerizability. The diallyl malononitrile does show spectral evidence suggesting that polarization of the α-CH_2 bonds should sufficiently decrease radical abstractability to allow propagation, a prediction supported by the formation of low molecular weight homopolymer. It is unexpected that the cyclization efficiency of this reaction should be so high (>90%), although it is not unreasonable that copolymerization with methyl acrylate (an inherently good monomer) leads to preferential incorporation of the acrylate and decreased cyclization efficiency. The thioether diacrylate, on the other hand, probes the ability of the methacrylate units to compete effectively for radical addition in the face of degradative chain transfer processes involving cleavage of the allyl thioether group; low molecular weight polymer formation indicates comparable rates. However, once intermolecular addition occurs, cyclization is again more than 90% efficient to give 6-membered ring repeat units containing the thioether moiety. These two examples, along with the recent increase in successful control of cyclization efficiency, ring-size, and polymer stereochemistry through a combination of steric, electronic, and mechanistic modifications, supports a resurgence in the use of cyclopolymerization of difunctional monomers to give novel and useful polymer structures.

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REFERENCES

[1] G. B. Butler, *Cyclopolymerization and Cyclocopolymerization*, Dekker, New York, 1992.
[2] T. Tsuda, and L. J. Mathias, *Macromolecules*, *26*, 4734 (1993).
[3] T. Tsuda and L. J. Mathias, *Ibid.*, *26*, 6359 (1993).
[4] T. Tsuda and L. J. Mathias, *Polymer*, In Press.
[5] S. Miyata, M. Yoshikawa, S. Tasaka, and M. Ko, *Polym. J.*, *12*, 857 (1980).
[6] V. P. Zubov, M. V. Kumar, M. N. Masterova, and V. A. Kabonov, *J. Macromol. Sci.—Chem.*, *A13*, 111 (1979).
[7] R. A. Vaidya and L. J. Mathias, *J. Polym. Sci.*, *Polym. Symp.*, *74*, 243 (1986).
[8] R. D. Thompson, W. L. Jarrett, and L. J. Mathias, *Macromolecules*, *25*, 6455 (1992).
[9] C. P. Jariwala and L. J. Mathias, *Ibid.*, *26*, 5129 (1993).
[10] L. J. Mathias, R. D. Thompson, and A. K. Lightsey, *Polym. Bull.*, *27*, 395 (1992).
[11] K. Chikanishi and T. Tsuruta, *Makromol. Chem.*, *81*, 198 (1965).
[12] J. Cheng, B. Yamada, and T. Otsu, *J. Polym. Sci.*, *Part A*, *Polym. Chem.*, *29*, 1837 (1991).