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Radical cyclopolymerization of sterically congested acrylic esters bearing bulky α-substituent containing allyl group

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Summary
Divinyl monomers consisting of an acryloyl group bearing large α-substituents containing allyl and methallyl groups were synthesized and their cyclopolymerizations were studied. Both monomers were found to be highly homopolymerizable to yield soluble polymers in solution or bulk. The formation of the highly cyclized polymers were confirmed by ^{1}H-NMR spectroscopy, although the size of the cyclic units could not be determined. The intramolecular addition of the acryloyl radical to the allyl or methallyl group is expected to form a six membered ring because of the steric hindrance to the formation of a five-membered ring.

Introduction

A variety of α-(substituted methyl)acrylates have been synthesized using α-(halomethyl)- or α-(hydroxymethyl)acrylic ester as the precursor, and the characteristics of their behavior during radical polymerization as a highly polymerizable monomer, effective chain-transfer agent, and polymerizable chain transfer agent have been reported (1). Among the α-(substituted methyl)acrylates bearing large substituents, methyl α-(2-carbomethoxyethyl)acrylate (MMEA) (2) and methyl α-[2,2-bis(carbomethoxy)ethyl]-acrylate (M(DM)EA) (3) are typical polymerizable monomers. However, ethacrylic ester shows extremely low polymerizability because of the steric hindrance of the α-ethyl group (4). A recent ESR study has revealed that the α-substituent of the polymerizable monomer simultaneously reduces the propagation rate constant (k_p) and termination rate constant leading to the favorable balance of slow propagation and termination for polymer formation and that the steric hindrance of the α-ethyl group of the ethacrylate reduces only the *k*p value to as small as those for MMEA and M(DM)EA in magnitude (5).

The polymer formation due to the balance of slow propagation and termination has been called "*ster¡c hindrance-assisted polymerization*" which is one of the useful concepts to produce the polymers from congested monomers (6). The extremely slow bimolecular reaction of the primary propagating radical from methyl α-[2,2,2-tris(carbethoxyethyl)]-acrylate (M(TE)EA) has also been known. However, M(TE)EA does not homo-polymerize as the steric hindrance of the α-substituent seems to exceed the limit for polymer formation (7). Furthermore, methyl α-[2-alkyl-2,2-bis(carbomethoxy)ethyl]-acrylate does not homopolymerize (8).

An alternative approach to polymer formation from a highly congested monomer is cyclopolymerization. Generally, a 1,6-diene monomer tends to simultaneously undergo cyclopolymerization and crosslinking. Crosslinking is effectively prevented when each counterpart of the diene does not homopolymerize, and as a result, a gel-free cyclopolymer

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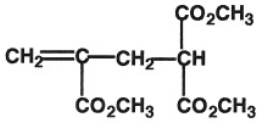
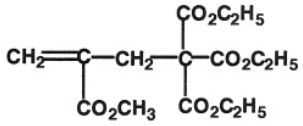
could be obtained. The cyclopolymerization of divinyl monomers derived from α-(hydroxymethyl)acrylate and α-(chloromethyl)acrylate has been studied by Mathias et al. (9-11) who have found efficient cyclopolymerization facilitated by steric hindrance to ordinary vinyl polymerization which would cause crosslinking. Thang and Rizzardo (12) have reported the efficient cyclopolymerization of methyl α-[2,2-bis(carbomethoxy)-2-(2'-carbomethoxyallyl)ethyl]acrylate to yield a soluble polymer. The cyclopolymerization of methyl α-(*N*-alkylallylaminomethyl)acrylate has also been reported (13). In this case, ring formation during propagation would not be disturbed because the α-(aminomethyl)-acrylate does not polymerize as well as allylamine. Replacement of one of the carbethoxy groups in the α-substituent of M(TE)EA by an allyl or methallyl group also gives the 1,6-diene monomer which fulfills the requirements for cyclopolymerization because the α-[bis(carbomethoxy)ethyl]acryloyl and allyl or methallyl groups do not independently homopolymerize.

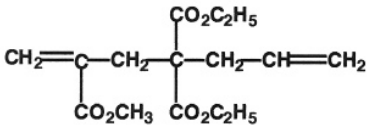
This work deals with the preparation and polymerization of two types of 1,6-dienes, methyl α-[2-allyl-2,2-bis(carbethoxy)ethyl]acrylate [M(DEA)EA] and methyl α-[2-methallyl-2,2-bis(carbethoxy)ethyl]acrylate [M(DEMA)EA]. The structures of M(DEA)EA, M(DEMA)EA, and related monomers are as follows:



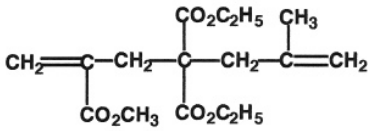
M(DM)EA



M(TE)EA



M(DEA)EA



M(DEMA)EA

Experimental

M(DEA)EA was prepared by the reaction of diethyl α-allylmalonate (30 g, 0.15 mol) with methyl α-(bromomethyl)acrylate(14) (MBMA: 27 g, 0.15 mol) in the presence of triethylamine (TEA: 16 g, 0.16 mol) in benzene. The reaction mixture was refluxed for 50 h, and the crude product was purified by distillation under reduced pressure. The structure and purity of M(DEA)EA were confirmed by ^{1}H- and ^{13}C-NMR spectroscopies. The y¡eld was 23.5 g (53%). During the distillation, 9 g (30%) of unreacted diethyl α-allylmalonate was recovered. M(DEA)EA: bp 120 °C/1 mmHg. ^{1}H-NMR ($CDCl_3$): δ = 1.26 (t, 6H, $CH_2C\underline{H}_3$), 2.60 (d, 2H, $C\underline{H}_2CH=CH_2$), 2.97 (s, 2H, $C=CCH_2O$), 3.72 (s, 3H, OCH_3), 4.16 (q, 4H, OCH_2), 5.10 (d, 2H, $CH=C\underline{H}_2$), 5.66-5.77 (m, 2H, $CH_2=C$, $C\underline{H}=CH_2$), 6.27 (s, 1H, $C=CH_2$). ^{13}C-NMR ($CDCl_3$): δ = 13.8 ($CH_2\underline{C}H_3$), 33.5 ($CH_2=C\underline{C}H_2$), 36.9 ($CH_2=CH\underline{C}H_2$), 51.7 (OCH_3), 57.3 (C), 61.0 (OCH_2), 119.0 ($CH=\underline{C}H_2$), 128.9 ($\underline{C}H_2=C$), 132.4 ($CH=\underline{C}H_2$), 135.8 ($CH_2=\underline{C}$), 167.1 ($\underline{C}O_2CH_3$), 170.3 ($\underline{C}O_2CH_2$).

M(DEMA)EA was prepared in a way similar to M(DEA)EA. Diethyl α-methallyl-malonate (20.0 g, 0.093 mol) was allowed to react with MBMA(14) (16.7 g, 0.093 mol) in

the presence of TEA (10.4 g, 0.103 mol) in the refluxed benzene for 50 h. Distillation under reduced pressure was carried out to isolate M(DEMA)EA. Its yield was 14.7 g (51%). Unchanged diethyl α-methallylmalonate, 8.2 g (41%), was recovered during the distillation. M(DEMA)EA: bp 130°C/1 mmHg. A preparative high-performance liquid chromatograph was used for the further purification of M(DEMA)EA. The structure and purity of M(DEMA)EA were verified by ^{1}H- and ^{13}C-NMR spectroscopies. ^{1}H-NMR ($CDCl_3$): δ = 1.23 (t, 6H, $CH_2C\underline{H}_3$), 1.69 (s, 3H, $CH_2=CC\underline{H}_3$), 2.69 (s, 2H, $C\underline{H}_2C(CH_3)=CH_2$), 3.01 (s, 2H, $CH_2=C(CO_2CH_3)C\underline{H}_2C$), 3.73 (s, 3H, OCH_3), 4.15 (q, 4H, OCH_2), 4.74 (s, 1H, $C\underline{H}_2=CCH_3$), 4.86 (s, 1H, $C\underline{H}_2=CCH_3$), 5.70 (s, 1H, $CH_2=C$), 6.26 (s, 1H, $CH_2=C$). ^{13}C-NMR ($CDCl_3$): δ = 13.8 ($CH_2\underline{C}H_3$), 23.6 ($CH_2=C\underline{C}H_3$), 34.2 ($CH_2=C(CO_2CH_3)\underline{C}H_2$), 40.9 ($CH_2=C(CH_3)\underline{C}H_2$), 51.8 ($OCH_3$), 56.7 (C), 61.3 ($OCH_2$), 115.0 ($CH_2CH_3=\underline{C}H_2$), 128.8 ($\underline{C}H_2=C$), 136.1 ($CH_2=\underline{C}$), 140.7 ($CH_2=\underline{C}$-$CH_3$), 167.5 ($\underline{C}O_2CH_3$), 170.9 ($\underline{C}O_2CH_2$).

2,2'-Azobisisobutylonitrile (AIBN, Wako) and 1,1'-azobiscylcohexane-1-nitrile (ACN, Wako) were commercially available and were recrystallized from methanol. Other reagents and solvents were commercially available and used as received or after ordinary purification. Polymerization was carried out in a glass tube sealed under vacuum. After a certain polymerization period, the polymerization mixture was poured into a large amount of *n*-hexane to isolate the polymer. Reprecipitation was then carried out to purify the polymeric product.

The ^{1}H- and ^{13}C-NMR spectra were recorded using a JEOL JNM A-400 spectrometer at 400 and 100 MHz, respectively. Deuteriochloroform and tetramethylsilane were used as the solvent and internal standard, respectively. The number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) were determined by a Tosoh 8000 series high-performance liquid chromatograph equipped with columns for gel-permeation chromatography (GPC) at 38 °C using tetrahydrofuran as the eluant; standard poly(styrene)'s were employed for calibration. ESR spectra were recorded on a Bruker ESP-300 spectrometer using a 5-mm o.d. quartz tube sealed under vacuum. The recycle type of preparative high-performance liquid chromatograph LC-908 (Japan Analytical Industry) equipped with JAIGEL-1H and 2H polystyrene gel columns using chloroform as the eluant was used for purification of the monomeric M(DEM)EA and M(DEMA)EA.

Results and Discussion

Any polymeric product of M(TE)EA was detected by GPC for the polymerization mixture after attempted polymerization for 10 h at 60 °C and the observed ESR spectra was assigned to the primary propagating radical (7). These findings suggest that the primary propagating radical consisting of an initiator fragment and one M(TE)EA unit does not propagate further. Homopolymerizability of the acrylic double bonds in M(DEA)EA and M(DEMA)EA seem to be extremely low because of their structural similarities.

The results of the homopolymerization of M(DEA)EA and M(DEMA)EA are summarized in Table 1. These monomers readily polymerized in solution to yield soluble polymers, the molecular weights of which are of the order of 10^4. Gelation was observed during the bulk polymerization of M(DEA)EA at high conversions and the intermolecular addition of the acyclic radical was shown to be involved in the propagation. However, the $\overline{M}_w/\overline{M}_n$ of the polymers of M(DEMA)EA increased from 1.8 at $\overline{M}_n$ = 30000 in solution to 3.6 at $\overline{M}_n$ = 72000 in bulk, and it seemed that a small amount of the pendant double bond

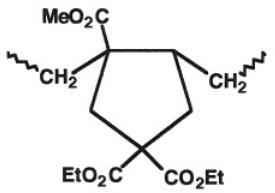
Table 1. Cyclopolymerization of M(DEA)EA and M(DEMA)EA at 60 ℃

Monomer	[Monomer] (mol/L)	Time (h)	Yield (wt-%)	Cyclization [c] (%)	$\bar{M}_n$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)
M(DEA)EA	1.0 [a]	6.0	61.6	97	12 000	3.3
M(DEA)EA	Bulk [a]	6.0	88.2	Gel	-	-
M(DEMA)EA	1.0 [a]	6.0	79.2	> 99	30 000	1.8
M(DEMA)EA	Bulk [b]	6.0	80.7	> 99	72 000	3.6
M(TE)EA	Bulk	10.0	0.0	-	-	-

a) Benzene solution at [AIBN] = 0.050 mol/L. b) [AIBN] = 0.016 mol/L. c) Determined by ^{1}H-NMR spectroscopy.

participated in branch formation. However, M(DEMA)EA did not crosslink even after bulk polymerization to high conversions. It was noted that the overall rates of polymerizations of these monomers are greater than that of styrene under comparable conditions whereas the individual carbon-carbon double bonds are less reactive than styrene.

Mathias et al. (10) have reported that the ether dimers of α-(hydroxymethyl)acrylates (CH_2=C(CO_2R)CH_2OCH_2C(CO_2R)=CH_2) bearing bulky ester alkyl groups tend to cyclopolymerize to soluble polymers in contrast to formation of crosslinked polymers from the lower alkyl esters of the ether dimer of the hydroxymethylacrylate. In these cases, the bulky ester alkyl group is expected to suppress the intermolecular propagation leading to the high efficiency of the cyclopolymerization. Considerable steric congestion around the acrylic and allylic double bonds is expected in M(DEA)EA and M(DEMA)EA, and ordinary vinyl polymerization of the acryloyl and allylic groups in these monomers seems to be too slow. Accordingly, the highly efficient cyclopolymerizations of M(DEA)EA and M(DEMA)EA are due, at least in part, to the steric hindrance of the bulky substituents.



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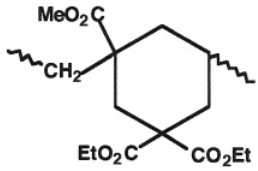

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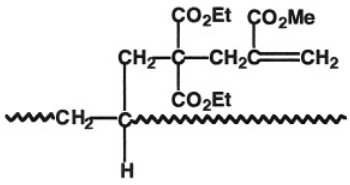

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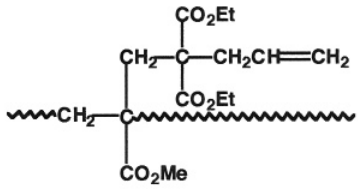

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The presumed structural units in the poly[M(DEA)EA] prepared by cyclopolymerization are shown by **1-4**. In accordance with the formation of the soluble polymers, only the extremely weak resonances assigned to the acrylic and allylic groups of **3** and **4** are found in the ^{1}H-NMR spectrum as shown in Fig. 1. Fig. 2 illustrates the expanded ^{1}H-NMR spectra of the olefinic proton regions with the assignments. The degree of cyclization determined from the intensity ratio of the resonances at 4.0-4.5 ppm due to the methylene protons in the ester alkyl group of the α-(substituted methyl)acryloyl unit to

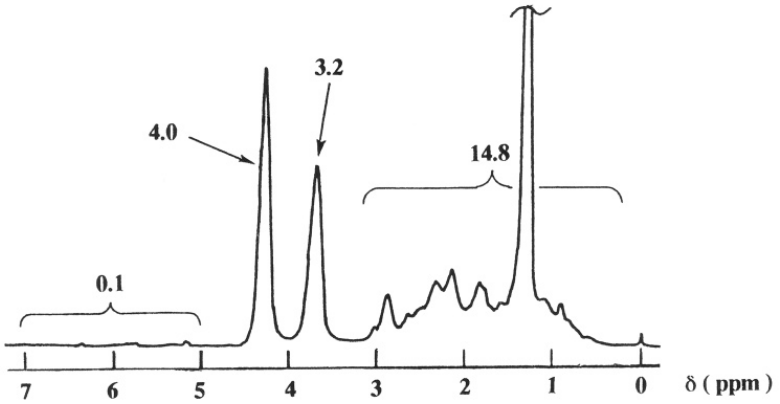


Fig. 1. ^{1}H-NMR spectrum of poly[M(DEA)EA]: $\bar{M}_n$ = 12000 ($\bar{P}_n$ = 40), $\bar{M}_w/\bar{M}_n$ = 3.3, conversion = 62%. Polymerization in benzene for 6 h at 60 ℃: [M(DEA)EA] = 1.00 mol/L, [AIBN] = 0.05 mol/L. Relative intesities are expressed in figures.

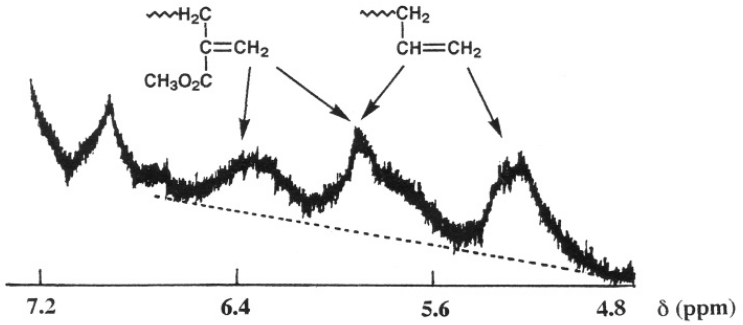


Fig. 2. ^{1}H-NMR spectrum of olefinic proton range of poly[M(DEA)EA]; --- shows the base line for intensity measurement.

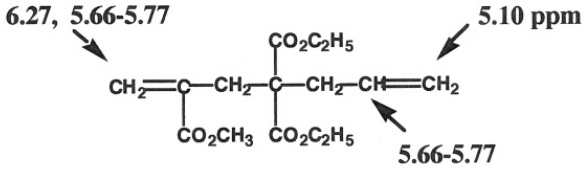


Fig. 3. Chemical shits of the olefinic protons of M(DEA)EA.

Table 2. Composition of pendant double bonds of poly[M(DEA)EA].

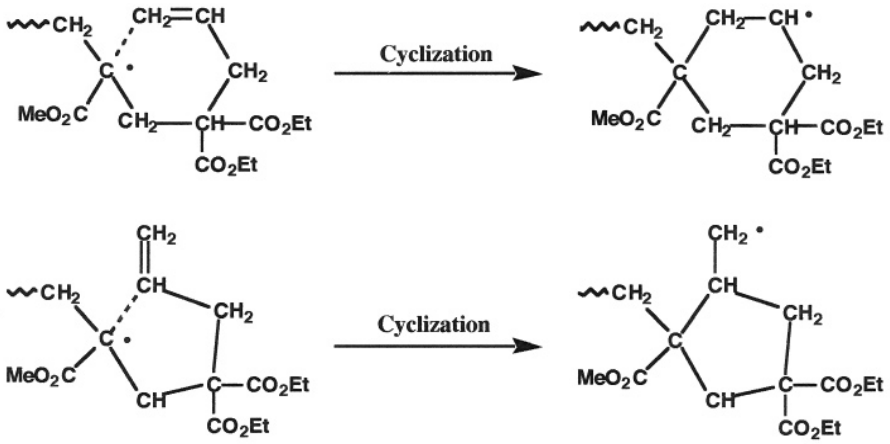
[M(DEA)EA] (mol/L)	[Initiator] (mol/L)	Time (h)	Temp. (℃)	Yield [a] (wt-%)	Cyclization [b] (%)	[Allyl] / [Acryl] [c]
1.0	AIBN, 0.05	6.0	60	61.6	97	60 / 40
0.2	AIBN, 0.05	15.5	60	31.8	>99	60 / 40
1.0	ACN, 0.05	1.0	80	20.2	99	24 / 76
1.0	ACN, 0.05	6.0	80	59.2	97	36 / 64

a) Insoluble in *n*-hexane. b) Determined by ^{1}H-NMR spectroscopy. c) The ratio of allylic to acrylic pendant double bonds.

those of the olefinic protons at 5.5-6.5 ppm was as high as 97-99%. A trace of the uncyclized unit is considered to cause the gelation during the bulk polymerization.

The content ratio of the allylic to acrylic double bonds as the pendant groups ([Allyl]/[Acryl) can be estimated from the intensity ratios among the resonances at 5.0-5.5, 5.5-6.1, and 6.1-6.5 ppm shown in Fig. 2. The resonances due to these olefinic protons are readily assigned because M(DEA)EA already has two types of unsaturated groups as shown in Fig. 3. It seems that the [Allyl]/[Acryl] ratio depends on temperature and an increase in temperature brings about a decrease in this ratio. Considering the small NMR signals but the comparable intensities, we can safely conclude that the acryloyl and allyl double bonds in M(DEA)EA exhibit similar reactivities in cyclopolymerization.

The five- or six-membered cylic unit could be formed as shown by Scheme 1. The ring size of the cylic structures from various difunctional monomers has been revealed by NMR spectroscopy. Mathias et al. (15) have shown that methyl α-(allyloxymethyl)-acrylate yields a polymer consisting of 5-membered repeating units through the cyclo-polymerization whereas various divinyl monomers have been known to form the repeating unit consisting of a six membered ring (9-11).



Scheme 1

The intramolecular addition of the acryloyl radical to the allyl or methallyl group is similar to the addition to the allyl group during the polymerization of methyl α-(allyloxymethyl)acrylate. However, the presence of biscarbethoxy group as a part of the α-substituent is expected to favor attack of the acrylic radical on the less hindered carbon of the allyl or methallyl group to form a six membered ring. The ^{13}C-NMR spectrum of the polymer from M(DEA)EA was also acquired. Although the spectrum was consistent with structures not having a pendant double bond, the complexity of the spectrum did not allow determination of the ring size.

Fig. 4 shows the ^{1}H-NMR spectrum of poly[M(DEMA)EA] prepared in solution. The polymerization of M(DEMA)EA gave a perfectly cyclized polymer which indicates over 99 % cyclization. Consistently, no resonance was observed in the chemical shift range from 5 to 7 ppm. The bulk polymerization of M(DEMA)EA produced a soluble polymer

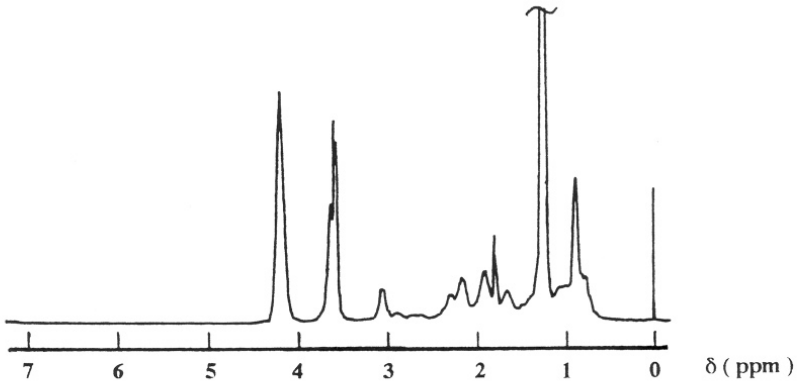
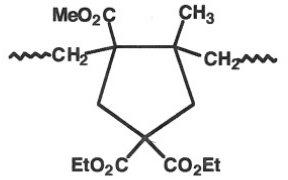


Fig. 4. ^{1}H-NMR spectrum of poly[M(DEMA)EA]: $\bar{M}_n$ = 30000 ($\bar{P}_n$ = 100), $\bar{M}_w/\bar{M}_n$ = 1.8, conversion = 79%. Polymerization in benzene for 6 h at 60 ℃: [M(DEMA)EA] = 1.00 mol/L, [AIBN] = 0.05 mol/L.



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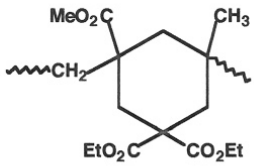

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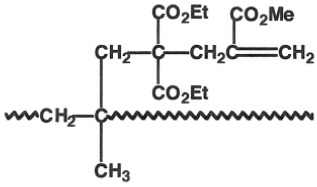

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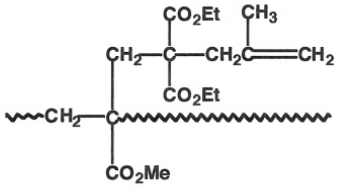

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whereas M(DEA)EA y¡elded insoluble polymers at higher conversions. The methallylic group of M(DEMA)EA effectively suppresses the intermolecular addition of the acyclic radical in comparison with the allyl group of M(DEA)EA. The preferential cyclization during the M(DEMA)EA polymerization can be explained by acceleration of the intramolecular addition to the methallyl group; the methyl group may contribute to the stabilization of the formed radical.

The presumed structures of the repeating units of poly[(M(DEMA)EA] are shown by **5-8.** Among these structures, the presence of uncyclized units **7** and **8** can be excluded because of the absence of the resonances due to the olefinic protons of **7** and **8** in the ^{1}H-NMR spectrum. As a result, the preference of the intramolecular and intermolecular additions to either the acrylic or allylic double bond could not be considered. Although the complexity of the NMR spectra did not provide any information about the size of the cyclic units, the six-membered ring seems to be preferable as already mentioned.

In conclusion, M(DEA)EA and M(DEMA)EA were found to yield their polymers readily via cyclopolymerization. Although the α-(substituted methyl)acryloyl group involved in both monomers is reluctant to ordinary polymerization, the severe steric congestion around the carbon-carbon double bond and the radical center of the propagating radical allow perfect cyclopolymerization. Furthermore, the methallyl group in the α-substituent facilitates more significantly the cyclopolymerization than the allyl group. The polymerizations of M(DEA)EA and M(DEMA)EA can be call *steric hindrance-assisted cyclopolymerization* as an alternative rout of *steric hindrance-assisted polymerization* to obtain polymer consisting of highly functionalized monomeric units. It is supposed that the cylopolymerization is not affected by ceiling temperature which reduces the polymerizability of some of sterically congested acrylic esters by raising temperature (3).

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