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Radical polimerization of methyl α-crotonyloxymethyl) acrylate to soluble polymer bearing pendant double bonds

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Abstract

Methyl α-(crotonyloxymethyl)acrylate (MCRMA) of which the α-substituted acryloyl and crotonyl groups are sterically hindered and reluctant to homopolymerize, respectively, was synthesized and polymerized. The polymerization of MCRMA primarily took place through homopolymerization of the α-(substituted methyl)acryloyl group to yield a soluble polymer bearing a large number of the pendant crotonyloxy groups. The ratio of the rate constants for the inter- and intramolecular additions of the propagating radical to form the linear and cyclic repeating units, respectively, indicates that this monomer exhibits an exceptionally low possibility of cyclopolymerization because of the sterically hindered intramolecular addition of the crotonyloxymethyloyl radical to the crotonyl group. Crosslinking by the reaction of the pendant double bond slowly proceeded due to an extremely low reactivity of the crotonyloxy group towards poly-[α-(crotonyloxymethyl)acrylate] radical.

Introduction

The radical polymerization of a monovinyl monomer usually produces a linear polymer consisting of a head-tail linkage of monomeric units. Cyclopolymerization in which each propagation step gives a cyclic unit is one of the most efficient structural controls for radical polymers. A variety of mainly non-conjugated 1,6-dienes have been subjected to cyclopolymerization to form polymers comprised of repeating unit involving five- and/or six-membered rings (1-3) as shown in Scheme I. The cyclopolymerization to a soluble polymers is required to take place alternative intermolecular and intramolecular additions of propagating radical. Therefore, one of the most important requirements for the monomer, which undergoes cyclopolymerization with quantitative cyclization, is suppression of the homopropagation of the individual double bonds.

N-Substituted dimethacrylamide (4-6) is a typical cyclopolymerization monomer in homo- and copolymerizations. Although *N*,*N*-disubstituted methacrylamide is reluctant to undergo homopolymerization involving the head-tail addition of the propagating radical to the monomer, the cyclopolymerization involving intramolecular addition to form the head to head linkage has been known to readily provide high molecular weight poly-(*N*-substituted dimethacrylamide). However, not very much types of monomers are

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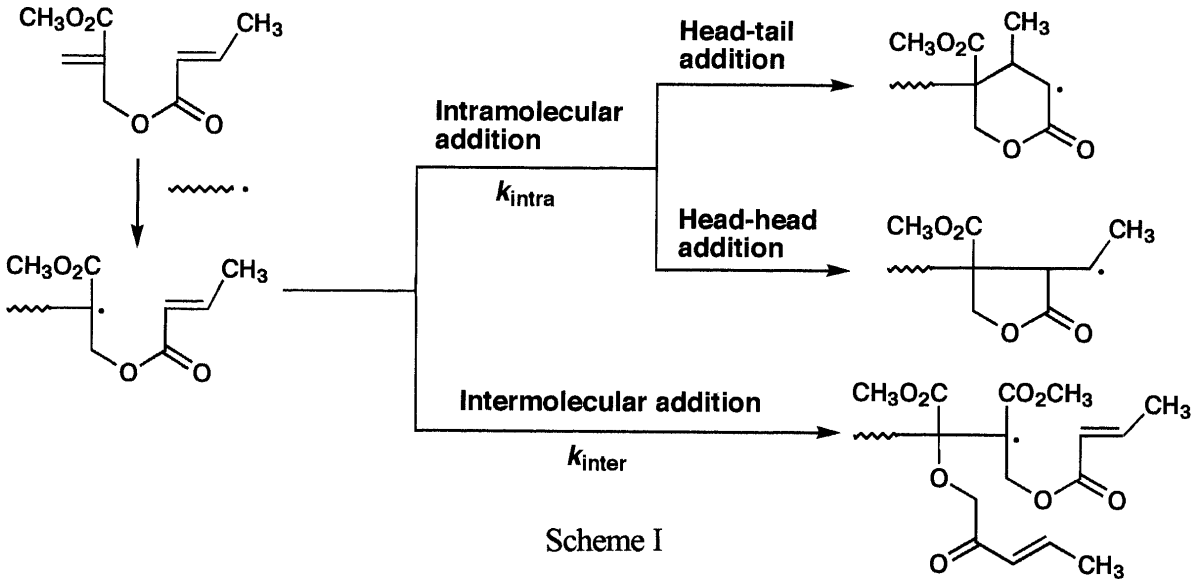
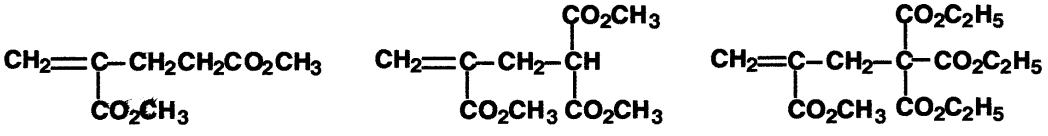


Scheme I

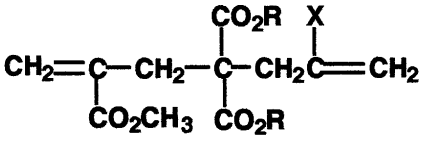
known as highly cyclopolymerizable monomers.

Methyl α-ethylacrylate is actually non-polymerizable monomer (7) whereas most of α-(substituted methyl)acrylates of which the α-substituents are larger than ethyl group readily yield high polymers as a result of the favorable balance of slow propagation and slow termination arising from steric hindrance (8). Mathias and Tsuda have synthesized cyclopolymerizable 1,6-dienes consisting of two of α-(substituted methyl)acryloyl moieties such as ether dimers of α-hydroxymethylacrylates bearing bulky ester alkyl groups (9) and dimethacrylmalononitrile (10). Kodaira et al. (11-13) have found that α-(*N*-substituted allylaminomethyl)acrylic esters cyclopolymerize to high molecular weight soluble polymers. Although the α-(*N*-substituted aminomethyl)acryloyl and allyl groups are not homopolymerizable, the cyclopolymerization containing them is allowed. Furthermore, a variety of 1,6-dienes involving the α-(substituted methyl)acryloyl group yield soluble polymers consisting of five- or six-membered repeating units as confirmed by ^{1}H- and ^{13}C-NMR spectroscopies or IR spectroscopy (14-19). It seems that the α-(substituted methyl)acryloyl group is one of the most beneficial components of the diene for cyclopolymerization.

In a series of studies of methyl α-(2-carbomethoxyethyl)acrylate **1** (20), methyl α-[2,2-bis(carbomethoxy)ethyl]acrylate **2** (21), and methyl α-[2,2,2-tris(carboethoxy)-ethyl]acrylate **3** (22), **1** and **2** were found to be homopolymerizable. Although the radical addition to **3** produced the corresponding primary propagating radical, the hindering α-substituent prevents further propagation to high polymer. Consequently, the primary propagating radical, **3**, is readily detected by ESR spectroscopy as a persistent radical. However, a non-conjugated 1,6-diene (**4**, R = CH_3 or C_2H_5, X = H or CH_3) obtained by replacement of one of the carboethoxy groups of **3** with an allylic group can cyclopolymerize to soluble high polymer (23). Apparently, the cyclopolymerization could overcome the steric hindrance which suppresses the vinyl polymerization.



1 **2** **3**



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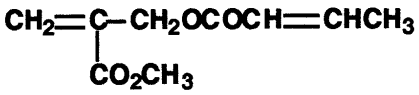


MCRMA

In the present paper, methyl α-(crotonyloxymethyl)acrylate (MCRMA) was synthesized and cyclopolymerized because the homopropagation of α-(substituted methyl)-acryloyl and crotonyloxy groups could be suppressed by steric hindrance fulfilling to the requirement for cyclopolymerization.

Experimental

MCRMA was prepared by the reaction of methyl α-(bromomethyl)acrylate with crotonic acid in the presence of triethylamine at room temperature with overnight stirring. The crude product was purified by recrystallization from benzene (yield, 32%). The structure and purity of MCRMA were confirmed by ^{1}H- and ^{13}C-NMR spectroscopies. ^{1}H-NMR (CDl_3): δ = 1.89 (d, 3H, C=CHC$\underline{H}_3$), 3.78 (s, 3H, OCH_3), 4.87 (s, 2H, OCH_2), 5.85 (d, 1H, C=CH_2), 5.90 (m, 1H, COCH), 6.37 (d, 1H, C=CH_2), 7.04 (m, 1H, C=C$\underline{H}CH_3$). ^{13}C-NMR: δ = 18.0 (CH=CHC$\underline{H}_3$), 52.0 (OCH_3), 62.1 (C=C(CO_2CH_3)-$\underline{C}H_2O$), 122.1 (CH=$\underline{C}HCH_3$), 127.3 (C=$\underline{C}H_2$), 135.3 (C=$\underline{C}$(CO_2CH_3)CH_2), 145.6 ($\underline{C}$H=CHCH_3), 165.7 (C=C($\underline{C}O_2CH_3$)CH_2), 165.8 (C=CHO$\underline{C}$O)

The polymerization of MCRMA was run in benzene at 60 °C, and 2,2'-azobis-isobutyronitrile (AIBN, Wako), which was purified by recrystallization from methanol, was used as the initiator. After the polymerization, the polymeric product was isolated using *n*-hexane as the precipitant. The ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM A-400 spectrometer; deuteriochloroform and tetramethylsilane were used as the solvent and the internal standard, respectively. IR spectra were taken using a JASCO FT/IR-200 spectrometer. The number and weight average molecular weight (M_n and M_w) were measured by a Tosoh 8020 series HPLC equipped with columns for GPC. THF was used as the eluant, and M_n and M_w were calibrated using standard polystyrenes.

Results and Discussion

Table I summarizes the results of the polymerization of MCRMA at different concentrations of monomer and initiator. All the polymers obtained were soluble in benzene indicating the absence of significant crosslinking.

Table I. Results of MCRMA polymerization under different conditions

[M] (mol/L)	[AIBN] (mol/L)	Time (h)	Convn. (%)	M_n (GPC)	f_c (NMR)
1.0	0.001	3	8.0	56800	0.031
1.0	0.001	24	52.3	73000	0.11
1.0	0.100	1	35.8	20600	0.18
0.5	0.001	6	9.6	24900	0.06
0.5	0.001	24	35.0	27300	0.15
0.1	0.001	48	23.0	2300	0.44
0.05	0.100	48	41.0	800	0.54

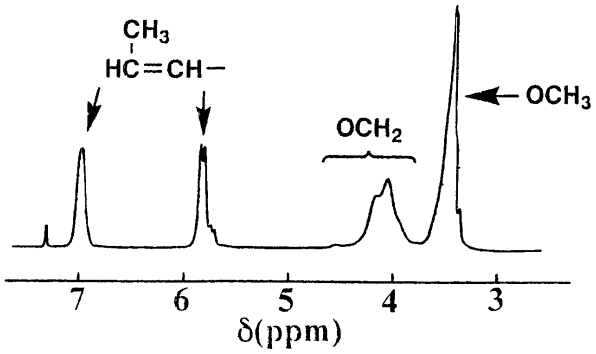


Fig. I. ^{1}H-NMRspectrum of poly(MCRMA) obtained by solution polymerizaiton in benzene at 60 °C: [MCRMA] = 2.0 mol/L and [AIBN] = 0.001 mol/L

Fig. I shows the ^{1}H-NMR spectrum of the polymer isolated. The resonances assignable to the methoxy (3.45 ppm) and methyleneoxy (4.05 ppm) protons, and the olefinic protons of the pendant crotonyloxy unit (5.85 and 6.95 ppm) are observed. Apparently, the polymer has a large number of the crotonyl double bond. The spectral intensity ratios of the resonance due to the olefinic protons to the methoxy protons indicate that < 1% of the cyclization took place during this polymerization. The resonances arising from the α-(substituted methyl)acryloyl group were not found in Fig. I although an expanded spectrum indicated the presence of only a small amount of the unchanged acryloyl group (< 0.5% relative to the crotonyl group).

Fig. II illustrates conversion-time and first order kinetic plots at different monomer concentrations. All the polymers obtained at 0.5 and 1.0 mol/L of [M] were soluble in benzene. However, insoluble polymers were formed at 2.0 mol/L at conversions higher than 40%. Linear relationships are obtained according to eq. 1 whereas the slopes of the plots are not the same at different monomer concentrations.

$$\ln[M]_0/[M] = k_p[M\bullet]t \qquad (1)$$

where [M•] denotes the concentration of the propagating radical. An increase in [M•] with an increase in [M] is anticipated otherwise the rate constant for propagation, k_p, should depend on [M]. Probably, the addition of the primary radical of the initiator became slower at a lower [M] as observed during the polymerizations of sterically congested monomers (24,25). The rates of polymerization of MCRMA calculated from the first order plots are 10^{-6}-10^{-5} mol/L·s, which are slower than that for methyl α-(acyloxymethyl)acrylate (26) by at least one order under comparable conditions.

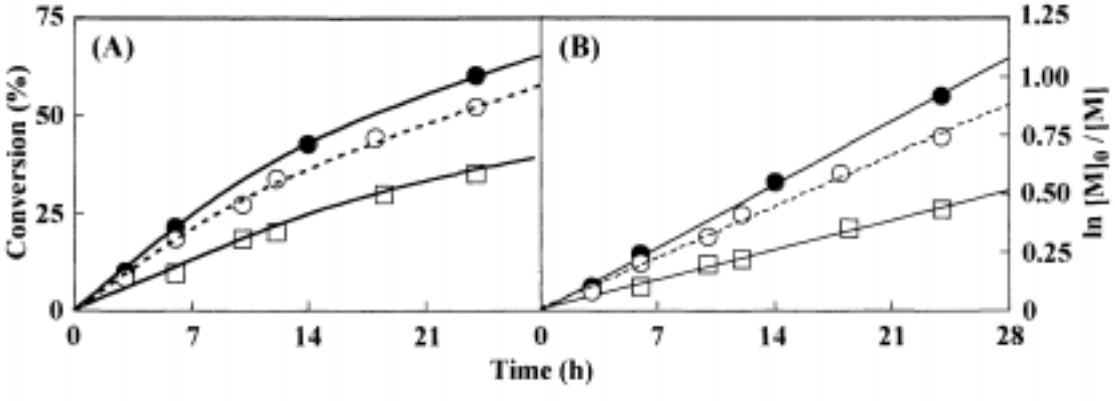


Fig. II. Conversion-time (A) and first order kinetic plots (B) for MCRMA polymerization at 2.0 (●), 1.0 (○), and 0.5 mol/L (□) concentration of monomer at 60 °C: [AIBN] = 0.001 mol/L

Extent of cyclization in percent was estimated as f_c which is given by eq. 2:

$$f_c = 100R_{intra} / (R_{intra} + R_{inter}) = k_{intra} / (k_{intra} + k_{inter}[M]) \qquad (2)$$

where k_{inter} and k_{intra} denote the rate constants for inter- and intramolecular additions of propagating radical. Considering the extremely low reactivities of crotonic ester in copolymerization, the intermolecular addition to the crotonyl double bond of MCRMA was ruled out for further consideration. f_c for MCRMA was evaluated using the ^{1}H-NMR resonances of the olefinic protons of the crotonyl group and methoxy protons of the carbomethoxy group. It was assumed that the pendant double bond is not consumed further by the reaction with propagating radical at a low conversion. The f_c values of MCRMA under different conditions were determined, and the ratio of k_{inter}/k_{intra} (= S) can be obtained as the slope of a plot shown in Fig. III according to eq. 3. The S value for MCRMA is compared with the values of some monomers in Table II.

$$1/ f_c = 1 + [M]k_{inter}/k_{intra} = 1 + [M]S \qquad (3)$$

In the case of the intermolecular propagation of the individual vinyl groups without cyclization, S should be infinitely large, and complete cyclization would result in S = 0. Methacrylic anhydride, acrylic anhydride, *o*-divinylbenzene, and the ether dimer of the methyl ester of which the S values are of the order of 10^{-2}-10^{-1} L/mol tend to form cross-linked polymers. The large S value, 11.2, has been evaluated for allyl methacrylate (27) which also readily produces the crosslinked polymer. On the contrary, monomers with

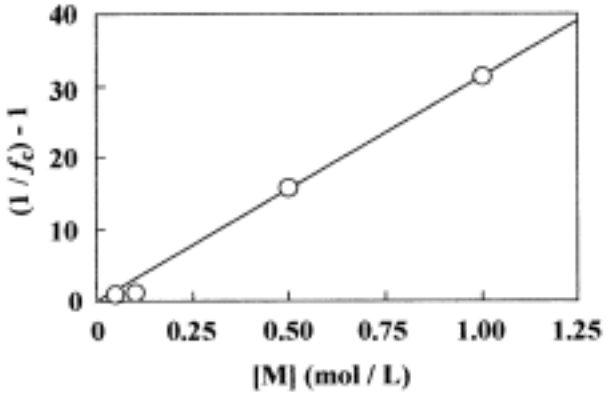


Fig. III. Plot of $(1/f_c) - 1$ versus [M] for determination of S

Table II. The values of S for MCRMA and other 1,6-dienes

Monomer	Solvent	Temp. (°C)	S (L/mol)	Ref.
MCRMA	benzene	60	31.2	This work
Acrylic anhydride	cyclohexane	45	0.17	5
Methacrylic anhydride	cyclohexane	37	0.022	5
o-Divinylbenzene	benzene	50	0.36	5
Ether dimer of methyl α-(hydroxymethyl)acrylate	benzene	50	0.060	8
Ether dimer of *tert*-butyl α-(hydroxymethyl)acrylate	toluene	50	0.011	8
Allyl methacrylate	benzonitrile	80	14.3	27

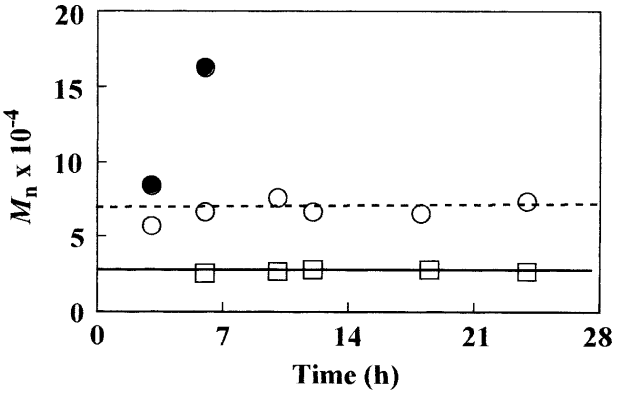


Fig. IV. Dependence of M_n on conversion for the polymerizaitons at 2.0 (●), 1.0 (○), and 0.5 (□) mol/L of MCRMA at 60 °C.

smaller S such as ether dimers of *tert*-butyl α-(hydroxymethyl)acrylate readily cyclopolymerizes via almost a complete cyclization. The large S value for MCRMA indicates that the intramolecular propagation is relatively slower than the intermolecular propagation. Noteworthy is the fact that the polymerization of MCRMA with such a large S value yields the soluble polymer. Suppressed crosslinking during the MCRMA polymerization cannot be quantitatively compared with that during the polymerization of allyl methacrylate. However, gelation during the MCRMA polymerization seems to be less preferred than that in the later based on the reported data.

Fig. IV shows that M_n of the polymer at different conversions remained almost constant at 0.5 and 1.0 mol/L, and the contribution of the reaction of the pendant double bond with a propagating radical to M_n can be ruled out. The pendant double bond is expected to exhibit a quite low reactivity towards the α-(substituted methyl)acryloyl radical due to the hindering β-methyl group. The polymerization at 2.0 mol/L of MCRMA gave crosslinked polymers after the rapid increase in M_n.

A decrease in [M] due to an increase in conversion would bring about a greater f_c as a result of the decrease in R_{inter}, and f_c at higher conversions can be given by eq. 4 by considering the effect of a decrease in [M] (28).

$$f_c = R/([M]_0 C) \times \ln([M]_0 + R)/([M]_0)(1 - C) + R) \qquad (4)$$

where C and R denote conversion and the ratio of k_{intra}/k_{inter} (= 1/S), respectively. Although the dependence of M_n on conversion (Fig. IV) suggested that further reaction of the pendant double bond with the propagating radical can be ruled out at 0.5 and 1.0 mol/L, Fig. V indicates an increase in f_c with increasing conversion. The effect of

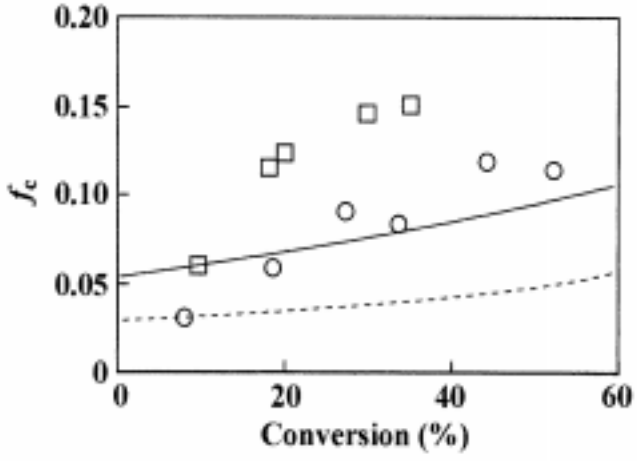


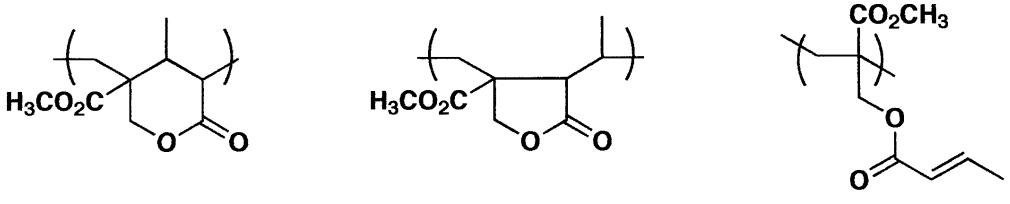
Fig. V. f_c of poly(MCRMA) obtained at 1.0 (○) and 0.5 (□) mol/L of monomer concentration at different conversions at 60 °C and theoretical curve calculated from eq. 4 at 1.0 (——) and 0.5 (----) mol/L

branched structure as a result of the reaction of the pendant double bond on M_n determined by GPC shown in Fig. IV could not be as sensitive as the change in the intensities of ^{1}H-NMR resonances.

^{13}C-NMR spectroscopy has been employed to determine the size of the cyclized unit based on comparison with a model polymer, and the six-membered cyclic unit of the ether dimers of α-(hydroxymethyl)acrylates (9) and dimethacrylmalononitrile (10) were confirmed. However, the spectrum of the poly(MCRMA) was too complicated for determination of the size of the cyclic unit. Another possibility to determine the ring size is based on dependence of $\nu_{C=O}$ of the lactone on the size of the ring structure. Stansbury (17) has shown the cyclopolymerzation of α-(methacryloyloxymethyl)acrylic ester to a soluble polymer cosisting of a δ-varelolactone unit evidenced by the absorption at 1735 cm^{-1}. Furthermore, Matsumoto et al. (27) have determined the contents of the cyclic units and pendant double bond in the polymers of methacrylic anhydride at different temperatures using IR spectroscopy.

The presumed structures of the repeating units are illustrated in Fig. VI. The IR spectrum of the poly(MCRMA) shown by Fig. VI exhibits an absorption at 1780 cm^{-1} together with a strong absorption at ca. 1735 cm^{-1}. The former is assigned to the $\nu_{C=O}$ of a γ-butyrolactone and the formation of cyclic unit can be confirmed. The $\nu_{C=O}$ of the δ-lactone might be hidden by the strong absorption of the $\nu_{C=O}$ of the pendant crotonyloxy group, and the formation of a six-membered cyclic unit cannot be ruled out.

Considering the intramolecular addition of the α-(crotonyloxymethyl)acryloyl radical to the crotonyl double bond, we can readily point out the steric hindrance of the β-methyl group of the crotonyl group to the head-tail addition and less stabilized radical formation by the head-head addition. The head-tail addition as the intramolecular addition seems not to be a slow process as can be seen from the polymerizable nature of



1735-1750 cm^{-1} 1760-1780 cm^{-1} 1700-1760 cm^{-1}

Fig. VI. Presumed structures of repeating units of poly(MCRMA) and $\nu_{C=O}$

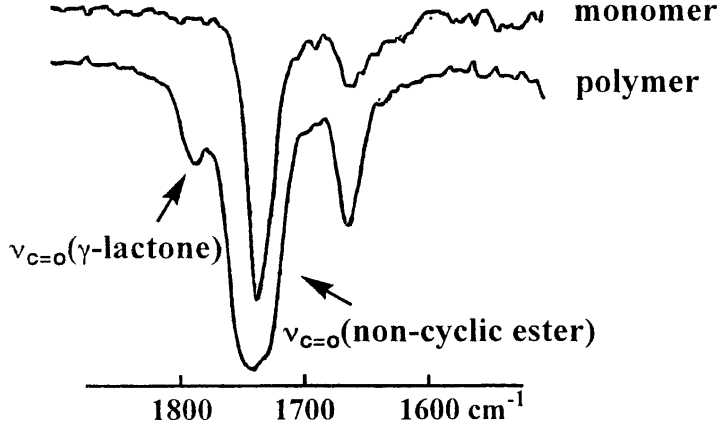


Fig. VII. IR spectra of monomeric MCRMA (above) and poly(MCRMA) (below). IR spectra were taken by KBr pellet method.

N-substituted dimethacrylamide, and the head-head addition resulting in the γ-lactone unit would primarily occur as intramolecular addition.

Conclusion

The polymerization of MCRMA can be characterized as slow intermolecular and intramolecular additions of the α-(crotonyloxymethyl)acryloyl radical leading to the low possibilities of cyclopolymerzation and further reaction of the pendant group. The quite unique MCRMA polymerization yields the soluble polymer bearing a large number of the pendant crotonyloxy groups; steric hindrance seems to govern the preferable reaction mode of either the intermolecular propagation or cyclopolymerization.

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