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Hydrogen Bonds of Poly[(*n*-alkyl methacrylate)-*co*-(methacrylic acid)]'s in Dilute Solutions

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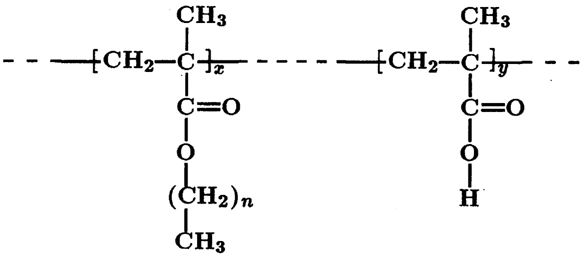
The nature of the association of poly[(*n*-alkyl methacrylate)-*co*-(methacrylic acid)]'s (poly(RMA-*co*-MAA)'s) in dilute chloroform solutions was investigated by Fourier transform infrared (FT-IR) spectroscopy and the solution viscosity. The proportions (P_{free}) of free carboxyls increased with the length of the alkyl groups in RMA's and with the decreasing MAA composition. From the relationships between P_{free} and the effective concentration (C_{eff}) of carboxyls attached to the polymer chain, it was shown that the major substituent effects of the alkyl groups on the hydrogen bonds in the copolymers are the extension of the polymer chain and the steric effect on the association between carboxyls and ester groups. Also, from the features of the shrinkage of the polymer chains accompanied with the intrachain association of carboxyls it was suggested that the hydrogen bonds in the copolymers are formed chiefly between neighboring sites along the chain.

The hydrogen bond is one of important intermolecular forces relating to the structures and properties of polymers. The introduction of hydrogen-bonding functional groups into the polymer chain is useful for the modification and functionalization of polymers and so understanding the relationships between the structures of hydrogen-bonding copolymers, and the natures of hydrogen bonds are of importance for the design and the processing of synthetic polymers. In particular, the study of hydrogen bonds in dilute solutions is necessary to realize the natures in thick solutions and the solid state.

The natures of the association of hydrogen-bonding copolymers in dilute solutions have been studied for copolymers of (meth)acrylic acid with styrene many times over the past years.[1—5] The recent basic studies for the association of hydrogen-bonding copolymers have been reported for model polymers modified using 4-phenyl-1,2,4-triazoline-3,5-dione (phenyl urazole) in relation to reversible gel formation.[6] However, no systematic study of the relationships between the structures and the natures of hydrogen bonds has been done, except for studies on the copolymers of methacrylic acid (MAA) with its methyl, ethyl, propyl, and butyl esters in the solid state.[7]

In this study, for poly[(*n*-alkyl methacrylate)-*co*-(methacrylic acid)]'s (poly(RMA-*co*-MAA)'s) with low MAA composition (Chart 1), the influences of the *n*-alkyl groups of RMA's on the intrachain association in dilute chloroform solutions were investigated by Fourier transform infrared (FT-IR) spectroscopy and the solution viscosity.



$$-\!\!-\!\!-[CH_2-C(CH_3)(C{=}O\,O(CH_2)_nCH_3)]_x-\,-\,-\,-[CH_2-C(CH_3)(C{=}O\,OH)]_y-\!\!-$$

$n = 0, 1, 2, 3, 5, 11, 17$

Chart 1.

Experimental

Materials. MAA and its methyl (MMA), ethyl (EMA), butyl (BMA), hexyl (HMA), dodecyl (DdMA), and octadecyl esters (OdMA), 2,2-dimethylpropanoic acid (DMPA), and ethyl acetate (EA) were purchased from commercial sources (Tokyo Kasei) and purified by distillation under atmospheric or reduced pressure before use. Propyl methacrylate (PMA) was prepared from MAA and propyl alcohol by the reported general method for preparations of RMA's.[8] 2,2′-Azobisisobutyronitrile (AIBN) (Nacalai Tesque) was reagent grade and purified by the recrystallization from methanol. Benzene as a polymerization solvent was purified by the ordinary method. Reagent grade chloroform was purified by passing through a column packed with alumina and used for the measurements of FT-IR spectra.

Polymerization. Copolymerizations of MAA with RMA's were done at total monomer concentration of 50 w/w% in benzene in the presence of AIBN (0.05 w/w%) at 60 °C under a nitrogen atmosphere. The degrees of conversion were always kept below 10%. The prepared polymers were purified by repeated reprecipitation from benzene to methanol. Poly(RMA)'s were similarly prepared and purified. Before use, the polymers were dried over diphosphorus pentaoxide in a vacuum oven for several days.

Composition of MAA in Copolymers. Compositions of MAA in copolymers were analyzed by titration in a benzene–methanol–$NaOCH_3$ system.

Averaged Molecular Weight. Gel permeation chromatography (GPC) was done with a Shimadzu LC-6A liquid flow unit, a Shimadzu RID-6A refractive index detector, a Shimadzu C-R4A chromatopack, and Shodex KF-800M and KF-800P gel columns, using tetrahydrofuran (THF) as an eluent solvent at a flow rate of 1 ml min^{-1} and at 40 °C. The weight averaged molecular weights ($\overline{M}_w$) were estimated by using the calibration curve of polystyrene standards. In general, the $\overline{M}_w$ values estimated for polymers other than the standard polymer differ from the absolute values and the comparisons among the different kinds of polymers are not pertinent even in a relative sense. However, for poly(MMA) and poly(OdMA) the ($\overline{M}_w$) values estimated by GPC measurements (4.6×10^5 for poly(MMA) and 15.0×10^5 for poly(OdMA)) were near to the viscosity-average molecular weights ($\overline{M}_v$) (5.4×10^5 for polyMMA and 15.9×10^5 for polyOdMA) determined from the intrinsic viscosities ([η]) in tetrahydrofuran and the known Mark-Houwink-Sakurada constants.[9)]

Also, for copolymers the $\overline{M}_w$ values estimated by the GPC measurements may be affected by the effects of the association of carboxyls on the coil dimension. However, the effects of the association are considered to be negligible in THF solutions, taking it into account that poly(BMA) and its partially hydrolyzed copolymer have nearly equivalent viscosities in THF[10)] and that poly(DdMA) and its partially hydrolyzed copolymer have nearly equivalent $\overline{M}_w$ in GPC measurements in this study.[11)] Thus, it seems that the $\overline{M}_w$ values estimated by the GPC measurements in this study are comparable to the absolute values.

The characteristics of prepared polyRMA's and poly(RMA-*co*-MMA)'s are shown in Tables 1 and 2, respectively.

FT-IR Spectroscopic Measurements. FT-IR spectra of chloroform solutions of polymers and low molecular weight compounds were measured on a Perkin–Elmer 1720X FT-IR spectrometer with NaCl cells (cell lengths of 0.1, 1, and 10 mm) at 25 °C.

The proportions (P_{free}) of free carboxyls in the copolymers were estimated from the integrated intensity of the OH stretching (νOH) band using the integrated molar absorption coefficient (A) of DMPA, a low molecular weight model compound of the carboxyl group in the copolymer. The estimation of the integrated intensity of the free νOH band in the copolymers was done for the spectra after subtraction of the spectra of poly(RMA)'s from those of the copolymers. The A value of the νOH band of free carboxyls of DMPA in chloroform was estimated as 5.0×10^6 cm mol^{-1} for the region of 3440—3560 cm^{-1}, based on the self-association constant (K_d), which was estimated as 1.9×10^2 mol^{-1} dm^3 from the concentration dependence of the intensity of the C=O stretching (νCO) bands of the dimeric and free carboxyls. Also, from the spectra of the mixture solution of DMPA and EA the association constant (K_x) between DMPA and EA was estimated as 8 ± 3 mol^{-1} dm^3.

Measurements of Viscosity. The viscosities of the chloroform and tetrahydrofuran solutions of polymers were measured with the Ostwald viscometer at 25±0.01°C. The [η] values were estimated from the data of the solutions in the concentration of ca. 0.2 g dl^{-1} by the method of the single point measurement.[12)]

Table 1. Characteristics of PolyRMA's

Polymer	$\overline{M}_w/10^5$	Polydispersity ($\overline{M}_w/\overline{M}_n$)
polyMMA	4.6	1.7
polyEMA	4.9	1.6
polyPMA	7.1	1.7
polyBMA	7.7	1.7
polyHMA	7.4	1.7
polyDdMA	8.1	2.0
polyOdMA	15.0	1.8

Table 2. Characteristics of Poly(RMA-*co*-MAA)'s

Copolymer	MAA/mol%		$\overline{M}_w/10^5$	Polydispersity
	Feed	Copolymer		($\overline{M}_w/\overline{M}_n$)
poly(MMA-*co*-MAA)	1.0	1.14	5.5	1.8
	2.0	2.65	5.5	1.7
	4.0	5.14	6.6	1.9
	6.0	7.77	7.9	2.2
poly(EMA-*co*-MAA)	1.0	1.79	5.3	1.7
	3.0	3.79	5.8	1.7
	4.0	4.94	6.7	1.5
	5.0	5.81	6.5	1.4
	6.0	6.72	6.7	1.7
poly(PMA-*co*-MAA)	1.0	1.02	6.8	1.8
	3.0	3.44	7.1	1.8
	4.0	5.51	8.1	1.7
	7.0	8.16	7.5	1.7
poly(BMA-*co*-MAA)	4.0	5.14	7.2	1.8
poly(HMA-*co*-MAA)	1.0	0.979	6.9	1.9
	2.0	2.15	6.7	1.9
	4.0	4.68	8.0	1.9
	6.0	6.98	7.0	1.9
	8.0	9.35	7.2	2.0
poly(DdMA-*co*-MAA)	4.0	5.06	13.1	1.8
poly(OdMA-*co*-MAA)	1.5	1.72	14.9	1.8
	3.0	4.74	13.7	1.9
	6.0	7.73	14.6	1.9
	9.0	13.9	16.0	1.8

Results and Discussion

Characteristics of Copolymers. The nature of the hydrogen bond in copolymers is considered to depend on various structural factors, such as composition, sequence distribution, tacticity, and molecular weight.

Although NMR spectroscopy is effective for the measurement of sequence distribution and tacticity,[13)] the analysis is difficult for copolymers without any appropriate peak for the measurement and for those with extreme compositions. Since the characteristics of copolymers are closely related to the production process, the differences in the characteristics among the examined copolymers were analogized from the monomer reactivity ratios in copolymerization.[14)] It is known that the steric effect of the ester alkyl groups on the radical copolymerizations of RMA's is small.[15)] So, it is considered that there is no appreciable difference in the sequence distribution and tacticity among poly(MAA-*co*-RMA)'s prepared by the radical copolymerization.

FT-IR Spectra of Copolymers in Dilute Solutions. The hydrogen-bond of poly(MAA-*co*-RMA)'s in solutions has never been studied. In the FT-IR spectra of poly(MMA-*co*-RMA)'s in chloroform, the analyses of the hydrogen bond were done for the νOH region, since the νCO bands of carboxyls could not be used for the analyses owing to the overlap with the strong bands of the ester carbonyl groups.

Although the region of 2500—3300 cm^{-1}, where the νOH bands of associated carboxyls are expected, was not well defined owing to the overlaps with the CH stretching bands of the RMA segments occupying most of the copolymers and with the bands of chloroform as a solvent, the region around 3500 cm^{-1}, where the νOH band of free carboxyls was expected by reference to the spectra of low molecular weight carboxylic acids in chloroform, were relatively well defined. FT-IR spectra in the region of 3150—3550 cm^{-1} of poly(RMA-*co*-MAA)'s with the MAA composition of about 5 mol% and poly(RMA)'s are shown in Fig. 1. In the spectra of the copolymers, two bands in 3420 and 3520 cm^{-1} were observed around 3500 cm^{-1}. The bands at 3420 cm^{-1} were observed for all poly(RMA)'s and low molecular weight aliphatic carboxylic acid esters. So, the bands in 3520 cm^{-1} could be assigned to the νOH band of free carboxyls and were used for the analyses of the association of the copolymers. The bands at 3420 cm^{-1} may be the overtone bands of the νCO bands observed at 1720 cm^{-1}.

The carboxyls in the copolymer may associate with ester groups of the RMA units in addition to the self-association. To discern the associations between carboxyls and ester groups in the copolymers and to recognize the characteristics in the association equilibria, the association between DMPA and EA, the low molecular weight models, was examined. The transformation in the FT-IR spectra of DMPA in chloroform accompanied by the addition of EA in 20-fold concentration, which corresponds to the molar ratio of RMA

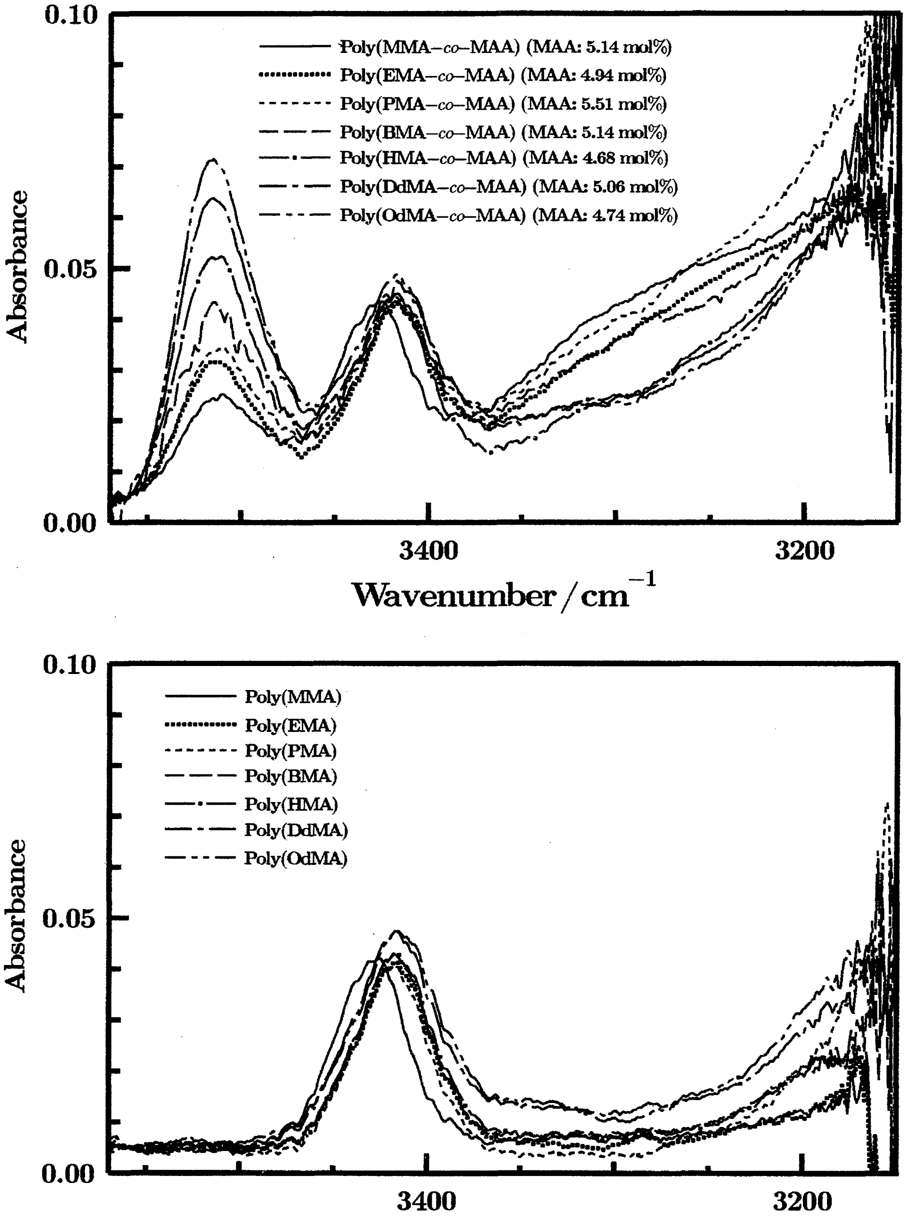


Fig. 1. FT-IR spectra of poly(MAA-*co*-RMA)'s with MAA composition of ca. 5% ([carboxyls] = 1×10^{-3} mol dm^{-3}) and poly(RMA)'s ([monomer units] = 2×10^{-2} mol dm^{-3}) in chloroform, measured with a 10 mm NaCl cell. The noisy region near 3150 cm^{-1} is the unmeasurable region due to strong bands of the solvent.

against MAA in the copolymer with the MAA composition of 5 mol%, are shown in Fig. 2. With the addition of EA, a broad band appeared around 3250 $\mathrm{cm^{-1}}$ and decreases in intensity of the free νOH band around 3520 $\mathrm{cm^{-1}}$ and the bands due to the self-associated carboxyls over the range of 2500—3000 $\mathrm{cm^{-1}}$ were seen. The broad band that appeared around 3250 $\mathrm{cm^{-1}}$ is thought to be the νOH band of the carboxyls associated with EA. Since the broad shoulder bands around 3300 $\mathrm{cm^{-1}}$ are observed for the spectra of copolymers with short RMA's in Fig. 1, it is shown that some carboxyls in copolymers form hydrogen bonds with ester groups.

It has been reported that for poly(styrene-*co*-MAA)'s the association in dilute 1,1,2,2-tetrachloroethane solutions is governed by the local concentrations of carboxyls in the individual chain.[1—3] This is also the case for poly(RMA-*co*-MAA)'s in this study, since the P_{free} values were nearly constant over the range of 1×10^{-3}—1×10^{-2} $\mathrm{mol\,dm^{-3}}$ in the stoichiometric concentration of carboxyls in the solution.

Substituent Effects of *n*-Alkyl Groups in RMA's on Association of Copolymers. The P_{free} values of the copolymers were estimated using the intensity of the νOH band of free carboxyls and the *A* value for DPMA. The relationships between the P_{free} values in the copolymers and the MAA composition are shown in Fig. 3. The P_{free} values

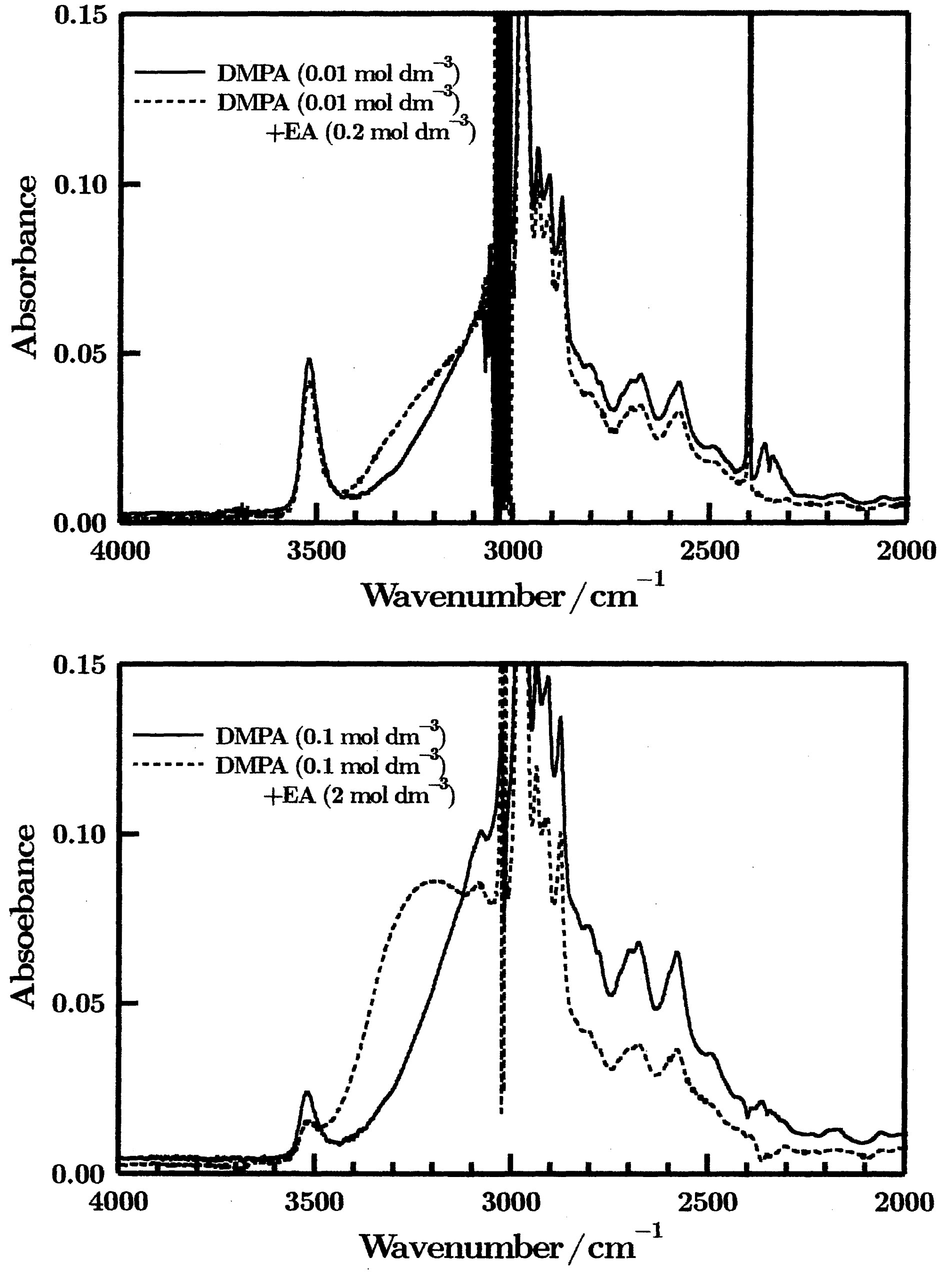


Fig. 2. FT-IR spectra of DMPA in chloroform and the transformation accompanied by the addition of EA, measured with a 1 mm NaCl cell for [DPMA] = 0.01 $\mathrm{mol\,dm^{-3}}$ and with a 0.1 mm NaCl cell for [DPMA] = 0.1 $\mathrm{mol\,dm^{-3}}$. The transformed spectra are given as the spectrum after subtraction of that of EA from that of the mixture of DPMA and EA. The noisy regions around 3000 and 2400 $\mathrm{cm^{-1}}$ are the unmeasurable region due to strong bands of the solvent.

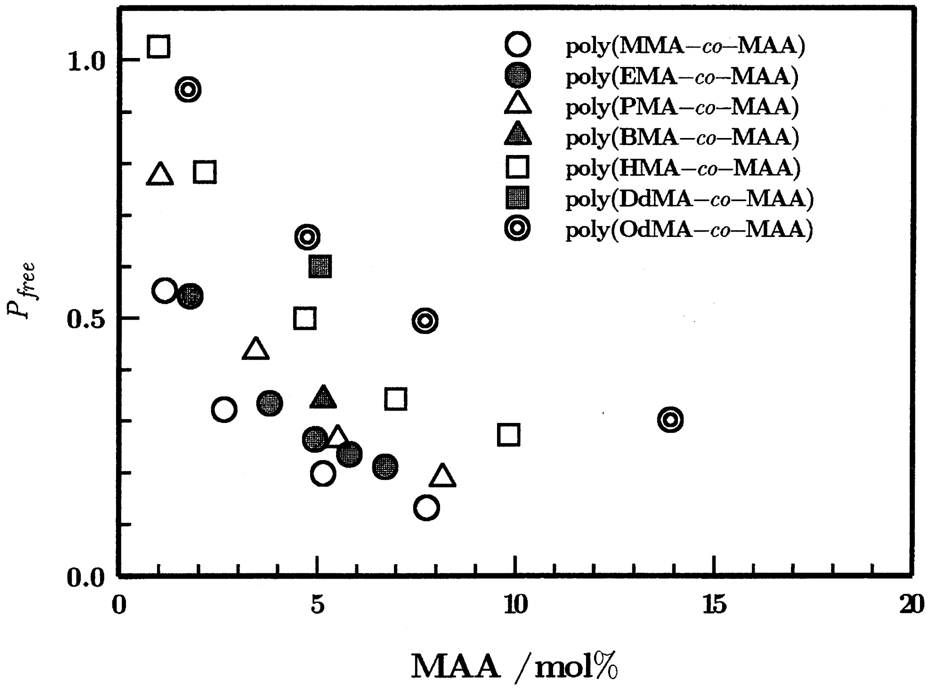


Fig. 3. Plots of P_{free} values in poly(MAA-*co*-RMA)'s vs. the MAA compositions.

increased with the alkyl chain length in RMA's. This feature has also been reported for the copolymers of MMA, EMA, PMA, and BMA in the solid state,[7] although the details of the substituent effects of the alkyl groups on the association have not been described.

It is thought that the principal influences of the ester alkyl groups on the intrachain association of the copolymers in the dilute solution are the expansion of the polymer coil through the effect on chain conformation and the steric hindrance of the associations. Since most of the chain in the examined copolymers is composed of RMA segments, the extension of the polymer coil may be appreciated by reference to the effects in the corresponding poly(RMA)'s. The properties of the extension of polymer coils are expressed in terms of Froly's characteristic ratios,[16] C_∞, defined as

$$C_\infty = \lim_{n\to\infty} \langle r^2\rangle_0 / nl^2,$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end distance in the 0 solvent, n the number of main-chain bonds, and l the bond length.

In the copolymers with the MAA composition of 5 mol%, the P_{free} values apparently correlate with the C_∞ values of the corresponding poly(RMA)'s,[17] as shown in Fig. 4. However, the steep decrease in P_{free} with the decreasing alkyl chain length of RMA's suggests that additional factors influence the association of the copolymers.

The coil dimensions of the copolymers in solutions are considered to be influenced by the swelling of the polymer coils in good solvents and the reduction in coil size, accompanied by intrachain associations in the copolymers.[1,4,10,18] The solvent effects of chloroform on the coil dimensions were evaluated for poly(RMA)'s in terms of $[\eta]_{\text{CHCl}_3}/[\eta]_\theta$, where the $[\eta]_\theta$ values were calculated using the equation,[19] $[\eta]_\theta = K_\theta M^{0.5}$ and the known K_θ values.[17] The results are shown in Table 3. Although the degree of swelling in chloroform increases with the decreasing alkyl chain length of RMA, the differences among poly(RMA)'s are not so great as to greatly alter the relative features in the coil dimension represented by C_∞.

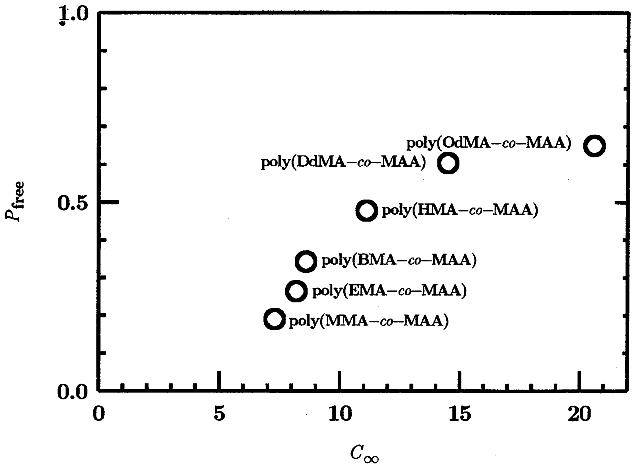


Fig. 4. Plots of P_{free} values in poly(MAA-*co*-RMA)'s with MAA composition of 5 mol% vs. C_∞ values of the corresponding poly(RMA)'s.

The shrinkage of the copolymers by the intrachain association was examined by the ratio (g) of $\langle r^2\rangle/n$ of the copolymer against that of the corresponding poly(RMA), that is

$$g = \frac{(\langle r^2\rangle/n)_{\text{poly(RMA-}co\text{-MAA)}}}{(\langle r^2\rangle/n)_{\text{poly(RMA)}}},$$

where n is the degree of polymerization and $\langle r^2\rangle$ is the mean

Table 3. Intrinsic Viscosities of Poly(RMA)'s in Chloroform and Solvent Effect on Coil Dimension

Polymer	$[\eta]_{\mathrm{CHCl_3}}$	$K_\theta{}^{\mathrm{a)}}/10^4$	$[\eta]_\theta$	$[\eta]_{\mathrm{CHCl_3}}/[\eta]_\theta$	$C_\infty{}^{\mathrm{d)}}$
poly(MMA)	1.70	4.9	0.33	5.2	7.3
poly(EMA)	1.58	4.8	0.33	4.8	8.2
poly(PMA)	1.74				
poly(BMA)	1.60	3.7	0.33	4.8	8.6
poly(HMA)	1.57	4.1	0.35	4.5	11.1
poly(DdMA)	1.34	3.5	0.32	4.2	14.5
poly(OdMA)	1.43	3.7	0.38	3.8	20.6

a) Taken from Ref. 16.

square end-to-end displacement, which is calculated by the Flory–Fox's equation[20] with intrinsic viscosity $[\eta]$ as follows,

$$\langle r^2\rangle = \left(\frac{M[\eta]}{\Phi}\right)^{\frac{2}{3}}$$

where Φ is a universal constant (2.1×10^{21}) and M the molecular weight of the polymer.

In the relationships between g and the MAA composition in Fig. 5, the degree of the shrinkage increased with the MAA composition and with the decreasing alkyl chain length of RMA. So, it is shown that the shrinkage is associated with the amount of the associated carboxyls.

Association Equilibria in Copolymers. The association equilibria of carboxyls in the copolymers were investigated by evaluating the effective concentration of carboxys (C_{eff}) in the polymer coil. C_{eff} was calculated according to the equation derived by Morawetz.[1,2] That is, on the basis of Kuhn's statics,[21] which represent the probability of ring formation of functional groups attached at a constant spacing along the polymer chain, C_{eff} is given by

$$C_{\mathrm{eff}} = \left(\frac{1000}{N_{\mathrm{A}}}\right)\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\langle m^2\rangle^{-\frac{3}{2}}f(z),$$

$$f(z) = \frac{2}{z}\sum_{j=1}^{j=z-1}\sum_{i=1}^{i=z-j} i^{\frac{3}{2}},$$

where N_{A} is Avogadro's number, $\langle m^2\rangle$ the mean square displacement of neighboring carboxyls on the copolymer and z the number of carboxyls on the polymer chain. $\langle m^2\rangle$ is calculated by

$$\langle r^2\rangle = \langle m^2\rangle z$$

The plots of P_{free} against C_{eff} are shown in Fig. 6. The plots for the copolymers with RMA's longer than HMA seem to be represented as a single function, but those for the copolymers with RMA's shorter than HMA are different functions from one another. These differences among the copolymers may be due to differences in the self-association constant (K_{d}) of carboxyls and/or in the association constant (K_{x}) of carboxyls with ester groups.

The association of carboxyls with ester groups was apparently observed for the copolymers with the shorter RMA's in the FT-IR spectra (Fig. 1). At a constant C_{eff} in Fig. 6, the concentration of the ester groups is higher in the copolymers with the shorter RMA's than in those with the longer RMA's, since the MAA composition in the copolymer is lower in the copolymers with the shorter RMA than in those with the longer RMA's. So, the low P_{free} value in the copolymers with the shorter RMA's might be due to the additional contribution of the association of carboxyls with ester groups. Also, for the copolymers with RMA's longer than HMA, it is shown that the P_{free} values approach 1 with decrease in C_{eff}. This means that the association of carboxyls with ester groups is negligibly weak.

The plots in Fig. 6 were simulated for the copolymers

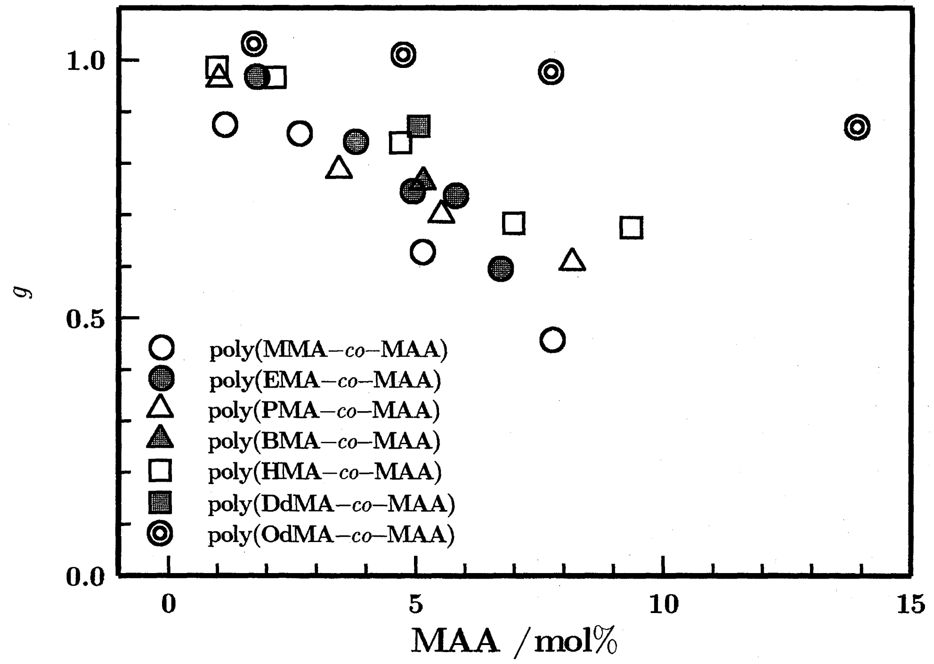


Fig. 5. Plots of g values of poly(MAA-*co*-RMA)'s vs. the MAA compositions.

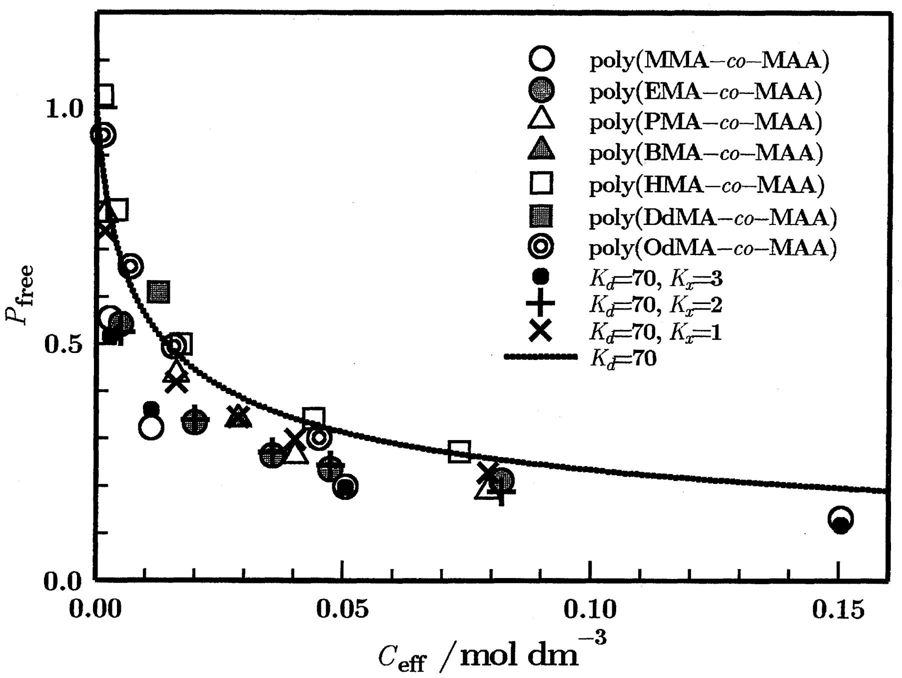


Fig. 6. The dependencies of P_{free} in poly(MAA-*co*-RMA)'s on the C_{eff} values and the simulated results using the assumed association constants (K_d and K_x).

with MMA, EMA, PMA, and BMA, taking into account the self-association equilibrium of carboxyls and the association equilibrium between carboxyls and ester groups, and for the copolymers with RMA's longer than HMA taking into account only the self-association equilibrium.

For the association equilibria consisting of only the self-association of carboxyls (A),

$$A + A \overset{K_d}{\rightleftharpoons} A_2$$

$$K_d = \frac{[A_2]}{[A]^2}$$

$$C_{eff} = [A] + 2[A_2]$$

P_{free} is given by

$$P_{free} = \frac{-1+\sqrt{1+8K_dC_{eff}}}{4K_dC_{eff}}.$$

On the other hand, for the equilibria consisting of the self-association and the association with ester groups (E),

$$A + A \overset{K_d}{\rightleftharpoons} A_2$$

$$A + E \overset{K_x}{\rightleftharpoons} AE$$

$$K_d = \frac{[A_2]}{[A]^2}$$

$$K_x = \frac{[AE]}{[A][E]}$$

$$E_{eff} = [E] + [AE].$$

P_{free} is given as a solution of the following equation,

$$2K_dK_xC_{eff}^2P_{free}^3+(2K_d+K_x)C_{eff}P_{free}^2+\{1+K_x(E_{eff}-C_{eff})\}P_{free}-1 = 0$$

where E_{eff} is calculated from C_{eff} and the mole fraction of MAA (f) as

$$E_{eff} = (f^{-1} - 1)C_{eff}.$$

The simulated P_{free} values are shown in Fig. 6, compared with the observed ones. For the copolymers with RMA's longer than HMA, the P_{free} values were reproduced using K_d of 70 mol^{-1} dm^3, and for the copolymers with MMA, EMA, PMA, and BMA using the K_d value and K_x values (mol^{-1} dm^3): poly(MMA-*co*-MAA), 3; poly(EMA-*co*-MAA), 2; and poly(PMA-*co*-MAA) and poly(BMA-*co*-MAA), 1. The estimated K_d and K_x values are apparently smaller than those in the low molecular weight molecules, although the ratios of K_x to K_d are comparable to that in the low molecular models. This may be due to the excluded-volume constrains[22,23] and/or the topological restriction[6] for the associations between segments on the chain.

The sequence of the increasing hindrance of ester *n*-alkyl groups for the association of carboxyls with ester groups in the copolymers, methyl < ethyl < propyl < butyl < hexyl ≈ dodecyl ≈ octadecyl, is similar to that for the steric hinderance of ester *n*-alkyl groups on hydrolysis of low molecular weight esters.[24] This appears to justify the idea that the association of carboxyls with ester groups is an important factor accounting for the influence of the alkyl groups on the intrachain association of poly(RMA-*co*-MAA)'s.

Intrachain Association and Shrinkage of Polymer Coils. The relationships between the shrinkage of polymer chains and the number of crosslinks by the intrachain association are closely related to the arrangement of the associating sites and to the form of polymer coils in the solvent.

The number of crosslinks by the association was estimated as the sum of half the number of the self-associated car-

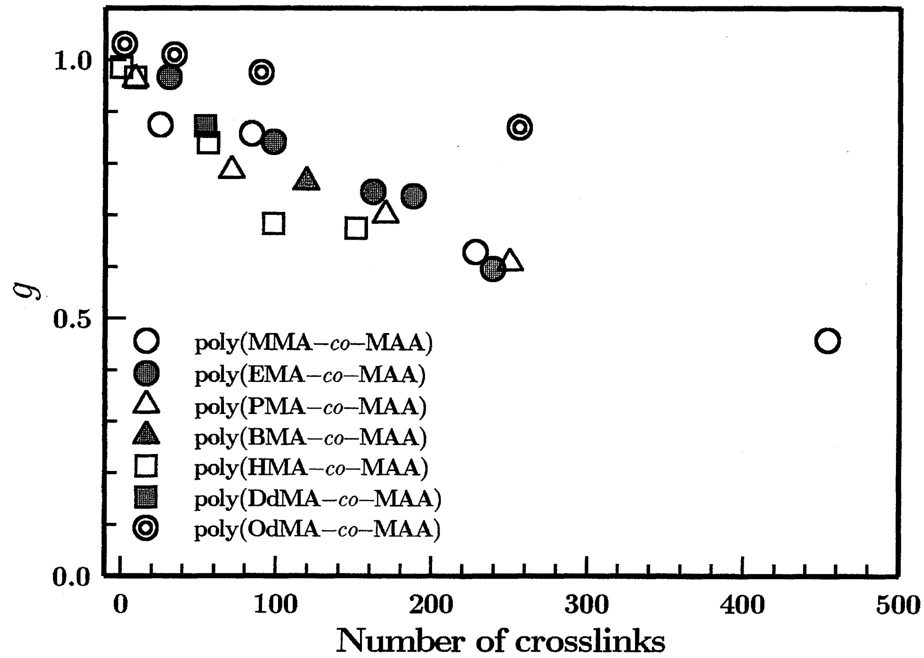


Fig. 7. Plots of g values of poly(MAA-*co*-RMA)'s vs. the number of crosslinks by the intrachain association.

boxyls and the number of carboxyls associated with ester groups and calculated based on the association equilibria described above. The relationships between g and the number of crosslinks are shown in Fig. 7. It is shown that g is linearly reduced with the number of crosslinks. The shrinkage of the polymer chain by intrachain crosslinking has been theoretically and experimentally studied.[22,25—27] Contrary to the theoretical predictions[22,26] the experimental results show a nearly linear relationship between the shrinkage and the number of crosslinks.[27] A monotonic decrease in the coil size with the number of crosslinks means that the associations occur chiefly between the neighboring sites on the polymer chain. The slopes of the plots of the copolymers, except for those in poly(OdMA-*co*-MAA), are nearly the same.

The crosslinks may occur between near neighboring sites, which are considered to be located dispersedly on the polymer chain for the copolymers with low MAA composition. If the loops formed by the crosslinks are small in the size and have no appreciable effect on the excluded-volume interaction, the chain size of the intramolecularly crosslinked polymer may be represented by that of the polymer shortened by the formed loops. Thus, the product of the slope and the degree of polymerization is approximately the length in the number of monomer units of the polymer chain reduced by a crosslink and is calculated as 8—10 monomers for the copolymers except for poly(OdMA-*co*-MAA). This result means that the distances between the associated sites along the polymer chain are nearly constant and independent of the MAA composition and the chain flexibility, and seems not to be explained on the basis of the statistical arrangement of the associated sites. The arrangement of the association sites with a nearly constant distance along the polymer chain might be formed during the copolymerization. The number of the reduced monomer units per crosslink seems to be reasonable for the shortening by the intrachain cyclization, taking it into account that the intramolecular association of α,ω-alkanedioic acids, $HO_2C(CH_2)_nCO_2H$ ($n = 4$—14), is possible for $n \geq 10$ and the feasibility rises with an increase of n up to 14.[28]

The gentle slope shown for poly(OdMA-*co*-MAA) could not explained by the formation of a small ring by the crosslink. Taking into account the fairly small proportion of the associated carboxyls and the chain rigidity in poly(OdMA-*co*-MAA), it is considered that the associations occur between a small number of the sites that can associate without any large chain transformation.

Conclusions

Poly(MAA-*co*-RMA)'s with low MAA composition in dilute chloroform solutions form self-associations of carboxyls and the association between carboxyls and ester groups in isolated polymer chains. Although the analyses used for the association equilibria in the copolymers contain some uncertainty in the C_{eff} values due to the method for the measurement of $\overline{M}_{\mathrm{w}}$ and due to the assumptions in the equations used, it was shown that the substituent effects of alkyl groups on the association are explained in terms of the effect on the effective concentration through the coil expansion and the steric effect on the association between carboxyls and ester groups. It seems that the steric hinderance of the ester groups against the self-association of carboxyls is negligible.

Also, for the copolymers except for poly(OdMA-*co*-MAA) it was shown that the intrachain associations chiefly occur between the neighboring ones with a nearly constant distance along the polymer chain, irrespective of the MAA composition and the chain flexibility.

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