

Hydrophobically modified polyelectrolytes

III. Reactivity ratio determination of FX14/AA, LA/AA and SA/AA

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The reactivity ratios of three hydrophobic monomers, FX14, LA and SA, to a hydrophilic monomer, acrylic acid (AA), were determined. For the fluorocarbon containing hydrophobic monomer FX14, elemental analysis was adopted to obtain the relative content of FX14 to AA. For two hydrocarbon monomers, ^{13}C NMR was used. FR, KT linear method and EVM nonlinear method were applied in calculating reactivity ratios. It is found that the reactivity of LA and SA is lower than that of AA, for solution polymerization in cyclohexane. Whereas FX14 is more reactive than AA in benzene. Finally, the distribution of small amounts of these hydrophobic monomers along the polymeric chain is discussed and a random sequence is confirmed.

Keywords Reactivity ratio, solution copolymerization, hydrophobic monomer, ^{13}C NMR

Introduction

Hydrophobically modified water-soluble polymers (HMWSP), which contain hydrophobic side chains along the hydrophilic backbones, have whetted both polymer scientists' and colloid scientists' interest for their unique rheological properties and prosperous applications in past two decades.¹⁻³ One of the usual methods in preparing HMWSP is solution polymerization in which two monomers with opposite solubility are cosolubilized. Obviously, it is indispensable to take the reactivity ratios of two monomers into account in the investigation of the structure-property relationship. However, until now the accurate copolymer composition is inscrutable and the

hydrophobic monomer is just arbitrated to be equal as the same as in feed, which joined into polymeric chains during polymerization.⁴

Another aim of the current study is to clarify the structure of HMWSP obtained by solution copolymerization. In Candau's opinion,⁴ evident hydrophobic association only results from blocky distribution of hydrophobic monomer along the polymeric chain which is produced under micellar copolymerization. While this opinion is in conflict with our experimental results that products from solution copolymerization can also induce strong association and at the same time solution copolymerization is suggested to bring with random distribution of hydrophobic monomer along the backbone when the feed ratio of hydrophobic monomer to hydrophilic monomer is small ($< 5\text{mol}\%$). Theoretic enforcement is needed for our finding. Nothing but reactivity ratios can tell us convincingly whether the distribution of hydrophobic groups along HMWSP is random or not in solution copolymerization.

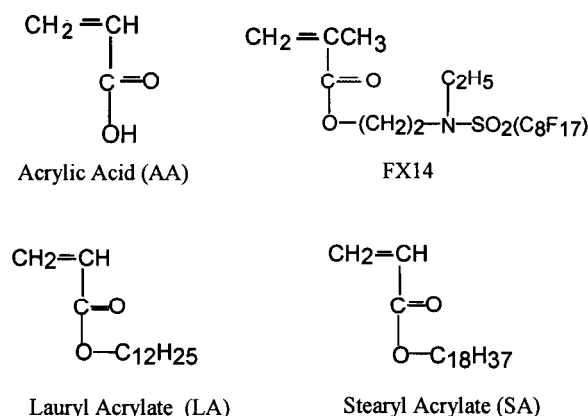
In our group acrylic acid (AA) is a monomer frequently used to construct hydrophilic backbone in preparing hydrophobically modified polyelectrolytes while lauryl acrylate (LA) and stearyl acrylate (SA) are two hydrophobic monomers. Although the reactivity ratios of LA and SA to acrylonitrile and vinylidene chloride were measured four decades ago,^{5,6} those to AA have not been covered so far partly because of the difficulty in measuring the composition of two monomers in the instantaneous copolymers only containing C, H and O.

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FX14 as an effective fluorocarbon-containing hydrophobic monomer was first used in the copolymerization with acrylamide by Zhang *et al.* 10 years ago,⁷ but the determination of reactivity ratios of these monomers with respect to AA has not been carried out. The structures of these four monomers are shown in Scheme 1.

Scheme 1 Structure of monomer and comonomers



High-resolution NMR spectroscopy has been not only extensively applied in the measurement of polymeric composition but also intensively used as a sensitive tool in the analysis of polymeric microstructure.⁸ In many cases, ¹³C NMR is more effective than ¹H NMR by the virtue of its broad chemical shifts. Recently Brar⁹ has made a compositional and stereochemical analysis for acrylamide/vinyl acetate copolymers by one- and two-dimensional NMR spectroscopy. The carbonyl carbon (> C = O) of both monomers can be respectively assigned by their chemical shifts. This is similar with our present systems in which there are two kinds of carbonyl carbons: from acrylic acid (AA) and from acrylate (LA, SA). Thus the ratio of two peak areas in NMR spectrum is regarded as that of the copolymer composition of two corresponding monomers. As for the copolymerization of AA and FX14, the copolymer composition is determined from the fluorine percent in the copolymers.

Experimental

Materials

Acrylic acid was distilled and stored below 5°C.

Lauryl acrylate (BASF) was washed with 10% NaOH prior to fractional distillation. Stearyl acrylate (BASF) was first dissolved in ethyl acetate and then washed as above, followed with the removal of the solvent. FX14 (3M) was recrystallized twice from methanol.

Preparation

A series of LA/AA, SA/AA, FX14/AA instantaneous copolymers containing different molar percents of LA, SA, FX14 were prepared by solution polymerization using AIBN as the initiator at 50°C. All the solution concentration was 20% (W/W). For LA/AA and SA/AA, the solvent was cyclohexane. Precipitation occurred in the copolymerization containing low feed contents of LA (10, 20, 40mol%) and SA (10, 20, 27.5, 31mol%) and the products were suctioned with diethyl ether, extracted with petroleum ether for 12 h, and dried at 50°C under vacuum overnight. When the feed content of LA (> 40mol%) and SA (> 31mol%) became high, no precipitation took place and the products were obtained by precipitating directly in methanol or first diluting with 1,4-dioxane and then precipitating in water, followed by extraction with methanol for 12 h and drying under vacuum. For FX14/AA, benzene was used as medium. Precipitation happened in all copolymerization with different feed contents. The products were suctioned and extracted with diethyl ether, and then dried as LA/AA and SA/AA. The percent conversion of all samples was kept below 10mol%.

Measurement

The copolymer compositions were calculated from the percent fluorine for the samples of FX14/AA. As to the samples of LA/AA and SA/AA, ¹³C NMR spectra were supplied. DMSO-D₆ was used as solvent for the samples LA-10, LA-20, LA-40, and SA-10, SA-20, SA-27.5, SA-31, while for the samples of high feed content of LA and SA, acetone-D₆ and the mixture of DMSO-D₆ and CDCl₃ (1:1/W:W) were used respectively. The control sample PAA was also solubilized in DMSO-D₆. Usually, a solution with high viscosity was afforded. The ¹³C NMR spectra for the samples of LA/AA and SA/AA were recorded at 45°C on a Bruker DPX 300-MHz spectrometer operating at 75.5 MHz. Proton inverse gated decoupling pulse sequence was used with a

20s relaxation delay. The relaxation delay was chosen as a compromise between total experimental time and quantitative accuracy. It was based on the fact that no large difference (< 5%) was observed in the relaxation delay between 20s and 60s, mainly due to the high viscosity and so that relatively short relaxation time.

Results and discussion

The compositions of FX14/AA copolymers were de-

termined from the percent fluorine of the copolymers while those of LA/AA and SA/AA copolymers were calculated from the peak areas of carbonyl carbon (> C = O) of the acrylates (LA, SA) and acrylic acid on the ¹³C NMR spectra. Results are listed in Table 1. Fig. 1 (a), (b), (c), (d) and (e) respectively show the typical ¹³C NMR spectra of PAA (homopolymer), LA-35, LA-65, SA-20 and SA-50. Doubtlessly, the signals around 176.0 should be assigned to the carbonyl carbon of acrylic acid while the carbonyl carbons of acrylates resonate around 174.1—174.6.

Table 1 Fractional composition of FX14, LA and SA in feed (f_1) and in copolymer (F_1) for the copolymerization with AA and the corresponding values for FR, KT, and EV M method^a

Samples	f_1 (composition)	F_1	X (EVM values)	Y	F (FR values)	G	ξ	η (KT values)
FX14/AA series ^b								
FX14-10	0.100	0.151	0.111	0.178	0.0695	-0.515	0.124	-0.920
FX14-20	0.200	0.288	0.25	0.405	0.154	-0.367	0.239	-0.570
FX14-35	0.350	0.490	0.538	0.962	0.301	-0.0212	0.381	-0.0267
FX14-42.5	0.425	0.539	0.739	1.167	0.468	0.106	0.489	0.110
FX14-50	0.500	0.508	1.00	1.031	0.970	0.0302	0.658	0.0211
FX14-72.5	0.725	0.737	2.636	2.804	2.478	1.696	0.835	0.572
FX14-80	0.800	0.823	4.00	4.636	3.451	3.137	0.876	0.796
LA/AA series ^c								
LA-10	0.100	0.0486	0.111	0.0511	0.241	-2.06	0.0867	-0.741
LA-20	0.200	0.111	0.250	0.125	0.500	-1.75	0.164	-0.576
LA-40	0.400	0.182	0.667	0.223	2.00	-2.29	0.441	-0.504
LA-50	0.500	0.224	1.00	0.289	3.46	-2.46	0.577	-0.410
LA-65	0.650	0.372	1.86	0.593	5.82	-1.27	0.622	-0.136
LA-80	0.800	0.476	4.00	0.907	17.64	-0.41	0.874	-0.0203
LA-90	0.900	0.751	9.00	3.02	26.84	6.02	0.914	-0.205
SA/AA series ^d								
SA-10	0.100	0.0408	0.111	0.0425	0.290	-2.50	0.157	-1.35
SA-20	0.200	0.0708	0.250	0.0762	0.820	-3.03	0.345	-1.27
SA-27.5	0.275	0.106	0.379	0.119	1.21	-2.81	0.437	-1.01
SA-31	0.310	0.142	0.449	0.165	1.22	-2.27	0.439	-0.817
SA-42.5	0.425	0.174	0.739	0.210	2.60	-2.78	0.625	-0.668
SA-50	0.500	0.221	1.00	0.284	3.52	-2.52	0.693	-0.496
SA-65	0.650	0.290	1.86	0.409	8.43	-2.68	0.844	-0.268

^a Polymerization was carried out at 50°, initiated by AIBN. ^b For KT method, $\alpha = (F_M F_m)^{0.5} = 0.490$. All products were precipitated from benzene. ^c For KT method, $\alpha = 2.54$. LA-10, 20, 40 were precipitated from cyclohexane. Others were soluble.

^d For KT method, $\alpha = 1.56$. SA-10, 20, 27.5, 31 were unsolvable for cyclohexane and others soluble.

According to the description considering the effect of only the last term of chain, the change in the composition of the copolymer in the copolymerization of two monomers can be expressed by the following Mayo-Lewis equation:¹⁰

$$dM_1/dM_2 = (M_1/M_2)(r_1M_1 + M_2)/(r_2M_2 + M_1) \quad (1)$$

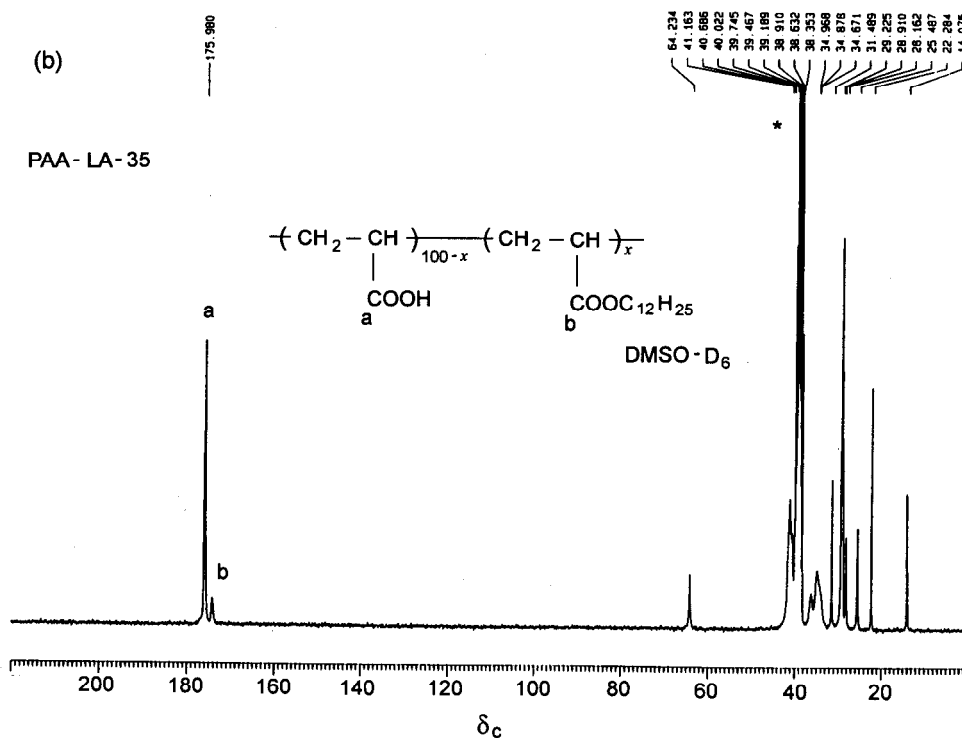
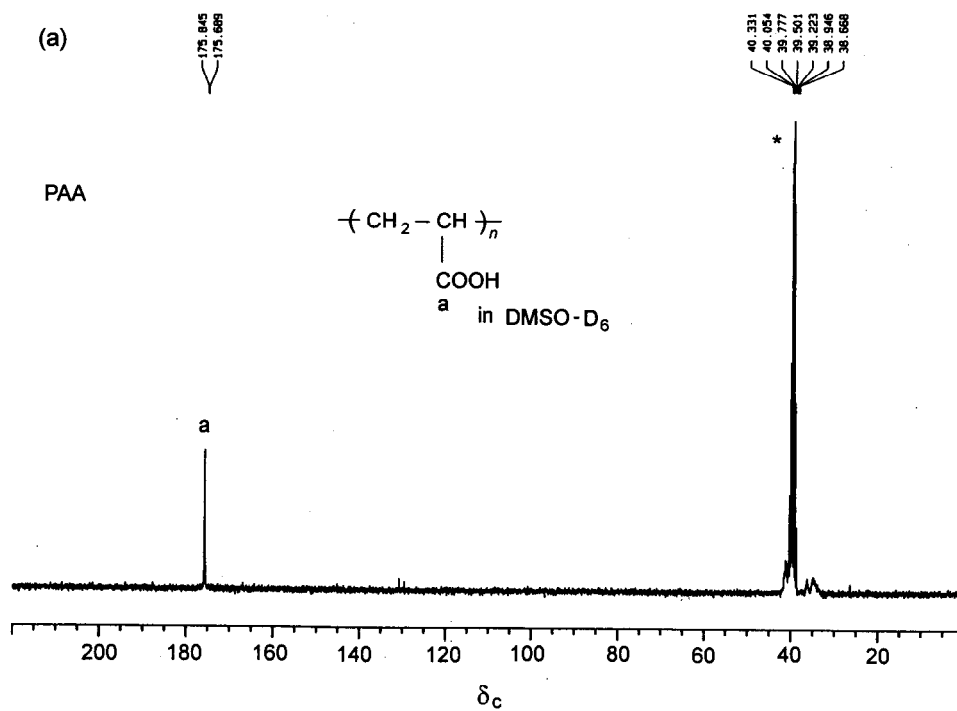
After introduction of $x = M_1/M_2$ and $y = dM_1/dM_2$, the following instantaneous compositional equation can be obtained:

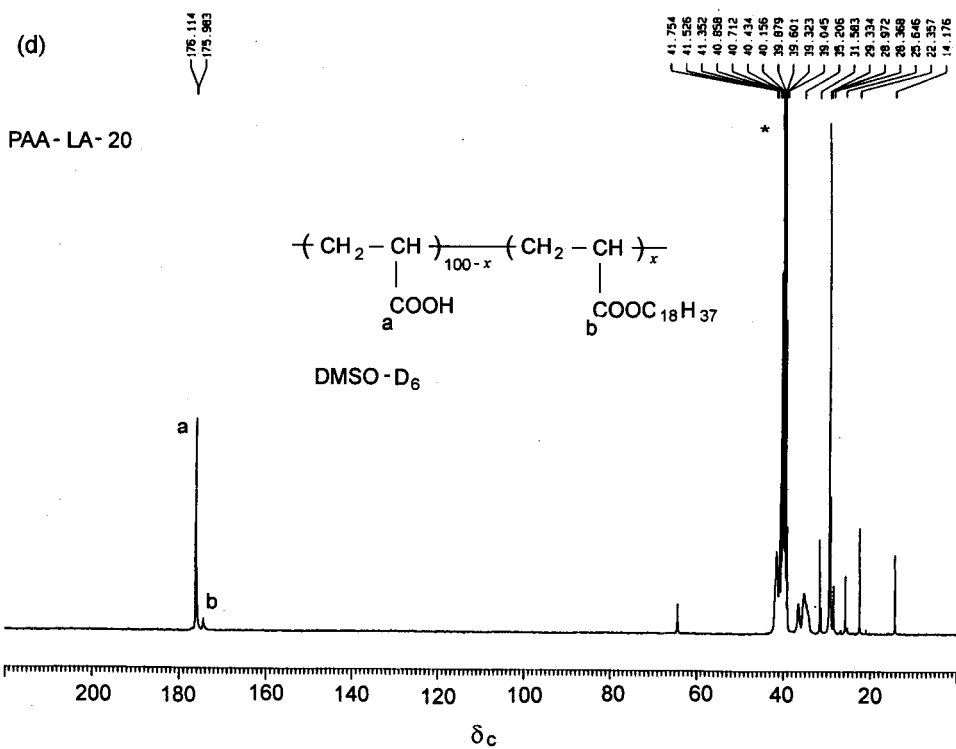
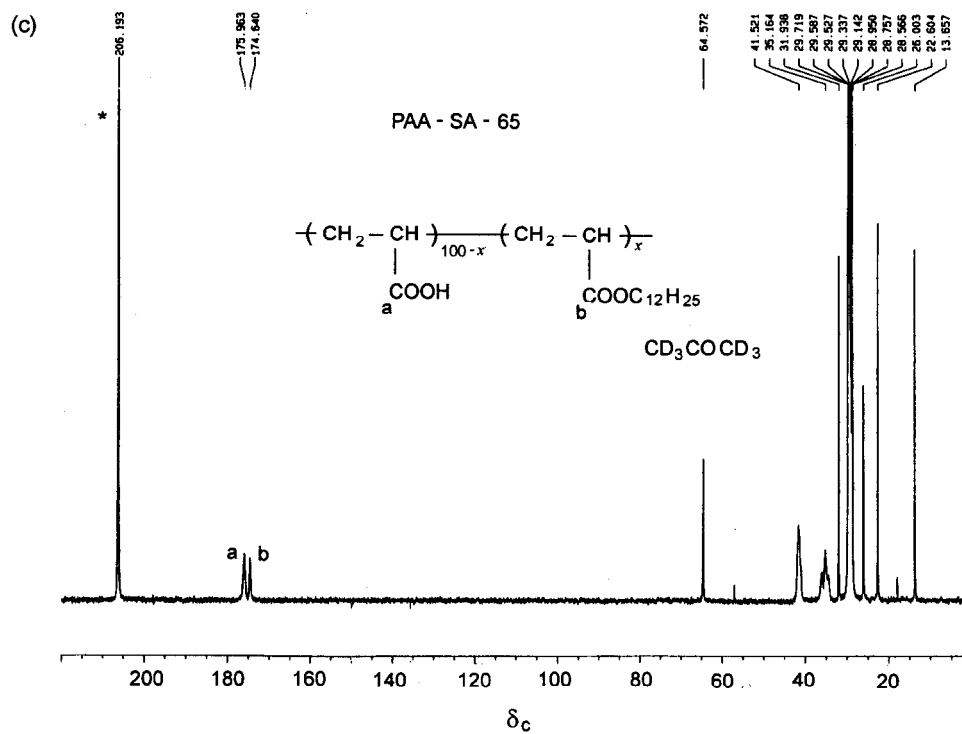
$$y = x(1 + r_1x)/(r_2 + x) \quad (2)$$

Eq. (2) was linearized by Fineman and Ross¹¹ as:

$$x(y - 1)/y = r_1x^2/y - r_2 \quad (3)$$

It can also be written as





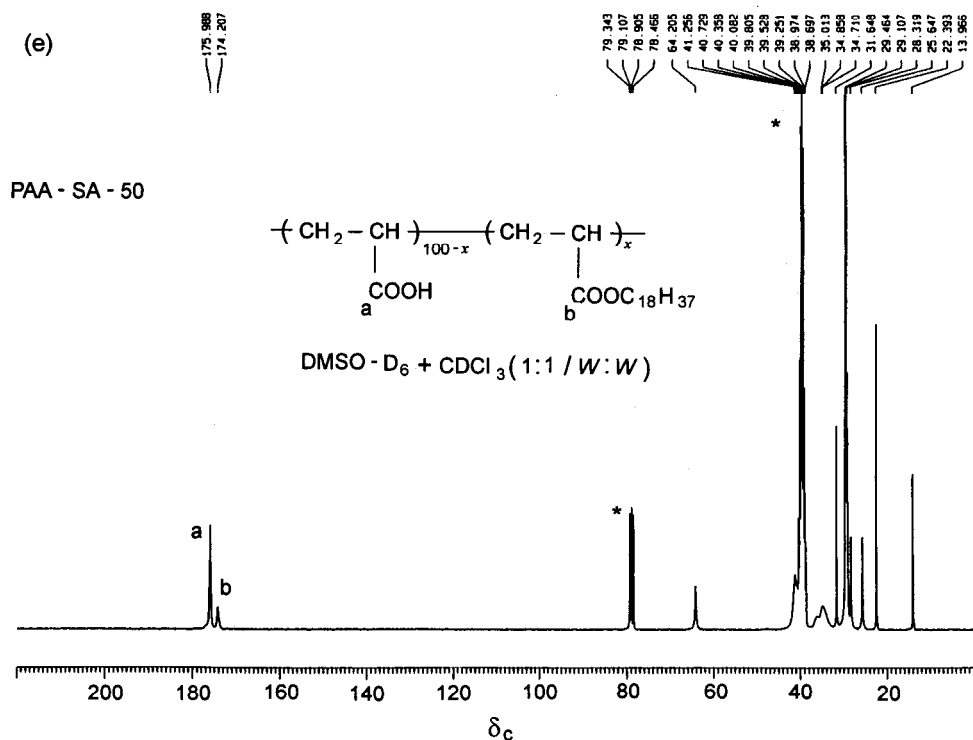


Fig. 1 ¹³C NMR spectra of PAA (a), LA-35 (b), LA-65 (c), SA-20 (d), SA-50 (e).

$$G = r_1 F - r_2 \quad (4)$$

where $G = x(y-1)/y$ and $F = x^2/y$.

Although FR method is widely applied, the experimental data are unequally weighted and the data obtained under extreme experimental conditions have the greatest influence on the slope of a line calculated by the usual linear least-squares procedure, as pointed out by Tidwell and Mortimer.¹² Another disadvantage of FR method showed by Kelen and Tudos¹² is that in case the copolymerization experiments are carried out by steadily changing the mole fraction $x/(1+x)$ of the comonomer mixture, the values calculated from the experimental data will appear along the ordinate at growing intervals.

Due to the above defects, FR method is being replaced by two new methods: improved linear graphic method by Kelen and Tudos¹² and nonlinear method by Behnken.¹³

In the case of KT linear method, equation (3) is refinedly linearized as:

$$G/(\alpha + F) = (r_1 + r_2/\alpha)F/(\alpha + F) - r_2/\alpha \quad (5)$$

where G and F hold the same meaning as in Eq. (4) and $\alpha = (F_M F_m)^{1/2}$. F_M and F_m stand for the highest and lowest value of F respectively. Eq. (5) can also be reduced as:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (6)$$

under conditions that $\eta = G/(G + \alpha)$ and $\xi = F/(F + \alpha)$.

In the case of nonlinear method, the extensive approach is to use the error-in-variable model (EVM) method,¹⁴ which correctly accounts for the error in both the independent and dependent variables. A computer program (RREVM) based on EVM method has been developed by Dube *et al.*,¹⁵ providing a convenient approach to the estimation of copolymerization reactivity ratios.

For the current three copolymerization systems discussed in this paper, KT method and EVM method are used for all. The errors in feed are controlled in 1%. The errors from copolymer composition are 5% for ¹³C NMR measurement and 1% for fluorine elemental analysis. Good linearity is also achieved in the application of FR methods to system of FX14/AA while poor linearity

results in the case of LA/AA and SA/AA. Therefore, the latter two lines are omitted.

All the variables and corresponding values used in the calculation by three methods are listed in Table 1. Fig. 2 shows the FR linear graph corresponding to the copolymerization of FX14/AA. In Fig. 3, the KT lines respectively correspond to the three copolymerization systems. The 95% confidence regions of the copolymerization of FX14/AA, LA/AA and SA/AA are drawn in

Fig. 4. The ultimate results of three sets of reactivity ratios are summarized in Table 2. It is obvious that for each copolymerization system, the reactivity ratios calculated by different methods are well in agreement with each other. This suggests that the results are convincing and compositional measurement using ^{13}C NMR as well as using conventional elemental analysis is feasible in determining reactivity ratios, especially for the conditions where elemental analysis is unavailable.

Table 2 Summary of reactivity ratios for the copolymerization of FX14, LA and SA with AA^a

	FX14-AA		LA-AA		SA-AA	
	r_1	r_2	r_1	r_2	r_1	r_2
FR	1.00 ± 0.08	0.55 ± 0.14	—	—	—	—
KT	0.96 ± 0.43	0.50 ± 0.08	0.16 ± 0.24	2.13 ± 0.23	-0.01 ± 0.03	2.63 ± 0.16
EVM	1.11 ± 0.06	0.56 ± 0.02	0.14 ± 0.05	2.17 ± 0.03	0.005 ± 0.06	2.65 ± 0.15

^a 95% confidence degree was met to evaluate the error region.

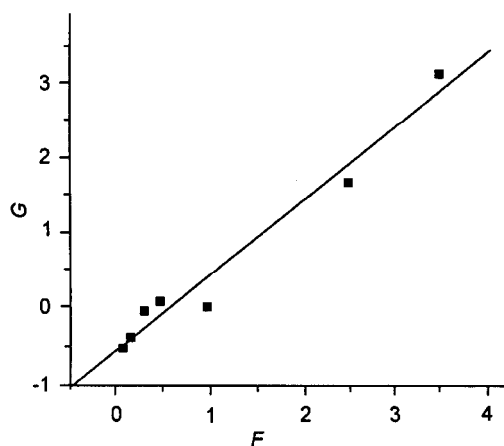


Fig. 2 Fineman-Ross graph for the copolymerization of FX14 with AA.

To all the three sets of reactivity ratios, there exists $r_1 r_2 < 1$ and it means they all belong to non-ideal copolymerization. For LA/AA and SA/AA, $r_1 < 1$, $r_2 > 1$ and $r_1 r_2 < 1$ mean they also belong to nonazeotropic copolymerization. While the copolymerization of FX14 and AA is between azeotropic ($r_1 = 0.96$, $r_2 = 0.50$ from FR method) and nonazeotropic ($r_1 = 1.11$, $r_2 = 0.56$ from EVM method). It also can be seen that the fluorocarbon-containing monomer FX14 is more active than two hydrocarbon monomers. The polarity effect may be responsible for the difference in reactivity ratios. In

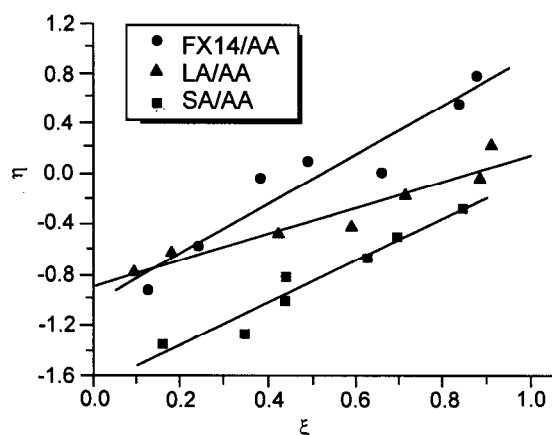


Fig. 3 Kelen-Tudos graph for the copolymerization of three sets of monomers.

FX14 the $-\text{N}(\text{C}_2\text{H}_5)\text{SO}_2\text{C}_8\text{F}_{17}$ group is a strong electron-acceptor and endows the acrylate more electric negativity as compared with long alkyl group in LA or SA, even though the group is separated with O by an ethylene group and the existence of α -methyl diminishes a little the electric negativity. That the reactivity ratios of SA is lower than those of LA is in coincidence with the results, presented by Tamikado and Iwakura in the investigation of the reactivity ratios of long-chain acrylic esters relative to acrylonitrile,⁵ that the longer the alkyl chain, the lower the reactivity ratios. For SA/AA, r_1 and r_2

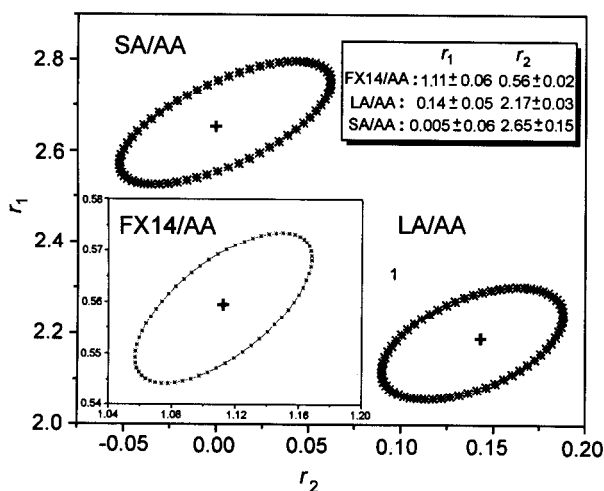


Fig. 4 EVM graph for the copolymerization of three sets of monomers.

obtained by the Price-Alfrey Q-e equation:¹⁶

$$r_1 = (Q_1/Q_2)\exp(-e_1(e_1 - e_2))$$

$$r_2 = (Q_2/Q_1)\exp(-e_2(e_2 - e_1)) \quad (7)$$

with $Q_1 = 0.83$, $e_1 = 0.88$ for AA and $Q_2 = 0.33$, $e_2 = 1.26$ ¹⁷ for AA are $r_{SA} = 0.25$ and $r_{AA} = 3.51$, respectively. This theoretical result is comparable with our

experimental result.

On the basis of Igarashi's representation of composition and blockiness of the copolymer:¹⁶

$$X = F_1 - 2F_1F_2/(1 + ((2F_1 - 1)^2 + 4r_1r_2F_1F_2)^{1/2})$$

$$Y = F_2 - 2F_1F_2/(1 + ((2F_1 - 1)^2 + 4r_1r_2F_1F_2)^{1/2})$$

$$Z = 4F_1F_2/(1 + ((2F_1 - 1)^2 + 4r_1r_2F_1F_2)^{1/2}) \quad (8)$$

where the fractions of the M_1-M_1 , M_2-M_2 , and M_1-M_2 bond in a copolymer molecule are denoted as X , Y , and Z respectively and F stands for the monomer content in copolymer. As indicated in Table 3, the probability of blocky sequence formed by a small amount of FX14, LA, SA is very low, even given that the feed ratio of these monomers reaches 10mol%. Therefore, the random distribution of small amount of hydrophobic monomer along the polymeric chain is confirmed. Thus, not only block distribution of hydrophobic side chain from micellar polymerization but also random distribution from solution polymerization can endow these polymer solutions strong associating ability.

Table 3 Copolymer composition for FX14/AA, LA/AA and SA/AA^a

Monomer 1	F_1	F_2	$X (M_1-M_1)$	$Y (M_2-M_2)$	$Z (M_1-M_2)$
FX14	0.151	0.849	1.6×10^{-2}	0.714	0.270
LA	0.0486	0.951	7.7×10^{-4}	0.904	0.096
SA	0.0408	0.959	2.5×10^{-5}	0.918	0.082

^a Provided that the molar fraction of monomer 1 is 10% and r_1r_2 is calculated from EVM.

Conclusion

By the way of fluorine elemental analysis and ¹³C NMR measurement, the reactivity ratios of one fluorocarbon-containing hydrophobic monomer FX14 and two hydrocarbon hydrophobic monomers LA and SA relative to AA were determined respectively. FR linear method, KT linear method and EVM nonlinear method are applied in calculating these reactivity ratios and the results are well in agreement with each other. The difference of polarity effect between fluorocarbon and hydrocarbon substituents and that of the alkyl chain length between LA and SA

are thought to be responsible for the fact that FX14 is far more active than LA and SA and the reactivity ratio of LA is somewhat higher than that of SA. The distribution of small amount of these hydrophobic monomer along the polymeric chain in solution copolymerization is confirmed to adopt a random sequence.

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