Acryloyl Chloride Polymer

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ABSTRACT: Free radical polymerization of acryloyl chloride (AC) was conducted in the following solvents: dichloroethane, ethyl acetate, tetrahydrofuran, dichloromethane, dioxane, and cyclohexane. However, poly(acryloyl chloride) with high molecular weights could be obtained only in solvent cyclohexane. The molecular weights of poly-(acryloyl chloride) could be measured through analogous poly(methyl acrylate). The reactivity ratios of AC (M_1) with styrene (St) or vinyl acetate (VA) obtained by the extended Kelen–Tüdös method at 42°C with dicyclohexylperoxydicarbonate as initiator in dioxane were found to be AC-St ($r_1 = 0.09 \pm 0.1$, $r_2 = 0.40 \pm 0.1$) and AC-VA ($r_1 = 0.84 \pm 0.1$, $r_2 = 0.03 \pm 0.1$), respectively. The Q and e values of AC calculated from obtained r_1 and r_2 were 0.58 and 1.02. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 665–670, 1998

Key words: acryloyl chloride; reactivity ratios; Kelen–Tüdös method; Q and e values

INTRODUCTION

During the past few years, a great deal of attention has been focused on functional polymers with special properties, such as pyroelectric properties,[1] photoconductive properties,[2,3] nonlinear optical properties,[4,5] and liquid crystal,[6,7] etc. Poly(meth)acrylates and poly(meth)acrylamides with various functional groups have been synthesized, but these functional groups often contain a number of groups (e.g., nitro or azo groups) that may act as retarders or inhibitors in free radical polymerization. Therefore, in many cases, the yields are not quantitative and the molecular weights are quite low.[8–11]

A novel method, the polymer analogous esterification or amidate of poly(methacryloyl chloride) and its copolymer, has been used for the preparation of polymethacrylates or polymethacrylamides with functional groups.[9–11] The free radical polymerization of methacryloyl chloride in 1,4-dioxane solution with azobisisobutyronitrile (AIBN) as initiator yields a high viscous solution from which the solid polymer is isolated by precipitation into dry hexane. In contrast, poly(acryloyl chloride) (PAC) forms a viscous oil when precipitated into hexane. Therefore, the 1,4-dioxane solution from free radical polymerization was used directly in the polymer analogous reactions.[11] Staudinger[12] tried to prepare PAC from poly-(acrylic acid) and thionyl chloride or phosphorous pentachloride, but obtained only insoluble, cross-linked material.

In this article, free radical polymerization of acryloyl chloride (AC) were conducted in different solvents, and solid polymers were obtained in cyclohexane. Furthermore, its reactivity ratios with styrene or vinyl acetate were also obtained by extended Kelen–Tüdös method.

EXPERIMENTAL

AIBN, benzoyl peroxide (BPO), and dicyclohexylperoxydicarbonate (DCPD) were recrystallized from methanol two times before use. All solvents

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Table I Polymerization of AC on Different Conditions

Run	Initiator	Solvent	[Monomer] (mol L^{-1})	$\frac{\text{[Initiator]}}{\text{[Monomer]}}$ (%)	Temperature (°C)	Time (h)	Yield (%)	M_η^a (×10^4)
1	AIBN	Dichloroethane	8.6	0.35	65	48	Oil	—
2	AIBN	Ethyl acetate	8.6	0.35	65	48	Oil	—
3	AIBN	—	—	0.70	65	48	Liquid	—
4	AIBN	Tetrahydrofuran	8.6	0.35	55	72	Oil	—
5	AIBN	Dioxane	8.6	0.35	65	48	Oil	—
6	DCPD	Dichloromethane	12.3	0.39	50	24	Oil	—
7	DCPD	Dichloroethane	12.3	0.45	50	24	Oil	—
8	DCPD	Tetrahydrofuran	12.3	0.28	50	24	Oil	—
9	BPO	Tetrahydrofuran	12.3	0.45	65	48	Oil	—
10	AIBN	Cyclohexane	4.9	0.39	70	6	62	1.49
11	AIBN	Cyclohexane	8.2	0.39	70	6	70	3.10
12	BPO	Cyclohexane	8.2	0.44	70	6	65	1.61
13	DCPD	Cyclohexane	8.2	0.37	55	2	63	1.27

^{a} Measured from poly(methyl acrylate) by equation[15] $[\eta] = 12.8 \times 10^{-3} M_\eta^{0.71}$ in benzene at 35.0°C.

were dried according to the literature.[13] Styrene and vinyl acetate were distilled under pressure. Infrared spectra of polymers were obtained with KBr on a FTIR-5DX spectrophotometer. Chemical shifts of monomer and polymer were obtained on a JEOL FX90Q.

AC monomer was obtained according to the literature.[14]

Polymerization of AC was conducted in a 100-mL three-necked bottle with a magnetic stirring bar under nitrogen atmosphere. Copolymerization of AC with styrene or vinyl acetate was performed in an ampulla under nitrogen atmosphere.

RESULTS AND DISCUSSION

Polymerization of AC

Strohriegl[11] has reported that PAC forms a viscous oil when precipitated into hexane with AIBN as initiator in dioxane. We thought it was because of the low molecular weights of obtained polymers; therefore, polymerization of AC was conducted on different conditions listed in Table I to obtain a solid polymer.

From Table I, it is difficult to obtain solid PAC by free radical polymerization in bulk or in solvents dichloroethane, ethyl acetate, tetrahydrofuran, dioxane, and dichloromethane; but, it was easy to obtain as a solid polymer in cyclohexane, the cause of which may be that cyclohexane is a bad solvent for AC and PAC, so gel effect exists during polymerization of AC, and a solid polymer with high molecular weight will precipitate from solution. Chemical shifts of monomer and polymer listed in Table II and infrared spectra of polymer shown in Figure 1(a) confirm that there is no chemical reaction of acryloyl groups during polymerization of monomer. Peak absorption at 1780 cm^{-1} indicates the existence of a carbonyl of AC.

Table II Chemical Shifts of AC and PAC

	δ (ppm)				
	^{1}H-NMR			^{13}C-NMR	
	—CH$_2$—	—CH—	—CH$_2$—	—CH—	—CO—
Monomer (CDCl$_3$)		6.0–6.8	136.8	133.1	166.3
Polymer (DMSO-d_6)	2.0–2.2	1.4	—	—	—

DMSO, dimethyl sulfoxide.

(a)

(b)
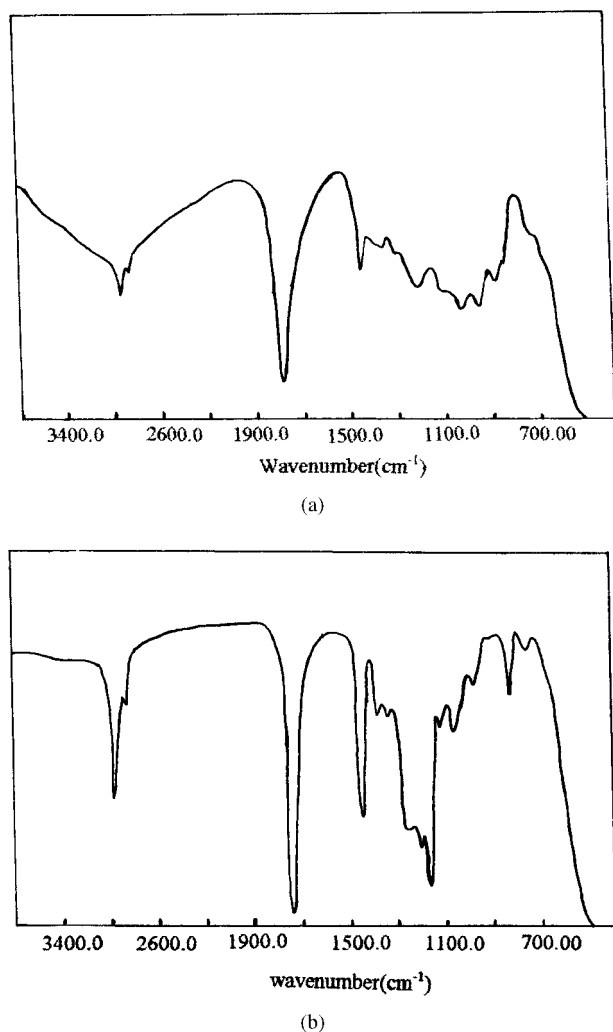
Figure 1 (a) Infrared spectra of PAC. (b) Infrared spectra of esterification product.

Polymer analogous esterification of PAC with absolute methanol was conducted at room temperature for 1 h. It is confirmed by infrared spectra shown in Figure 1(b) and NMR (chemical shifts are listed in Table III) that the esterification product is poly(methyl acrylate), which has no difference with polymer obtained by free radical polymerization of methyl acrylate monomer. Direct measurements of PAC molecular weights are

Table IV Critical f_1 from Different Q and e Values

		AC–Styrene		AC–Vinyl Acetate	
Q	e	f_1'	f_1''	f_1'	f_1''
1.82[22]	1.92[22]	0.995	0.030	0.861	0.001
0.85[23]	1.58[23]	0.990	0.081	0.749	0.002
1.780[24]	1.020[24]	0.878	0.061	0.169	0.001

difficult to perform because of its active reactivity; thus, we can modify PAC with a 100% yield by absolute methanol to give poly(methyl acrylate) and measure the molecular weights of analogous poly(methyl acrylate).

Copolymerization of AC with Styrene or Vinyl Acetate

Copolymerization with other monomers is an effective method to modify the property of polymer, so reactivity ratios of monomer are essential parameters. Usually, the reactivity ratios r_1 and r_2 are obtained from some version of the Mayo–Lewis equation[16]:

$$\frac{F_1}{F_2} = \left(\frac{f_1}{f_2}\right) \frac{r_1 f_1 + f_2}{r_2 f_2 + f_1} \quad (1)$$

where f_i represents the mole fraction of monomer i in the reaction that is instantaneously producing copolymer containing mole fraction F_i of monomer i. This equation relating F_i to f_i is nonlinear in r_1 and r_2, but can easily be manipulated into linear forms by defining new dependent and independent variables that are functions of f_1 and F_1. McFarlane and coworkers[17] have compared the precision of estimation of copolymerization reactivity ratios by different methods and concluded that, for a new monomer pair, a linear method such as that of extended Kelen–Tüdös[18–20] may be used.

Table III Chemical Shifts of Esterification Product of PAC with Methanol

NMR	^{1}H-NMR (CDCl$_3$)			^{13}C-NMR (CDCl$_3$)			
Group	—CH—	—CH$_2$—	CH$_3$—	—CH—	—CH$_2$—	CH$_3$—	—CO—
δ (ppm)	1.6–1.8	2.2–2.4	3.65	35.2	41.4	51.8	174.9

Table V Copolymerization of AC (M_1) and Styrene (M_2) at 42°C Initiated by DCPD ([Initiator] = 2.66×10^{-2} mol L^{-1})

Run	$[M_1]_0 + [M_2]_0$ (mol L^{-1})	f_1	f_2	Time (h)	Yield (%)	F_1[a]	F_2
1	10.61	0.857	0.143	7	45	0.605	0.395
2	10.74	0.647	0.353	5	40	0.488	0.512
3	10.65	0.502	0.498	5	48	0.425	0.575
4	10.94	0.342	0.658	5	30	0.376	0.634
5	10.69	0.150	0.850	7	20	0.240	0.760

[a] Calculated from polymer(methyl acrylate-co-styrene) by ^{1}H-NMR.
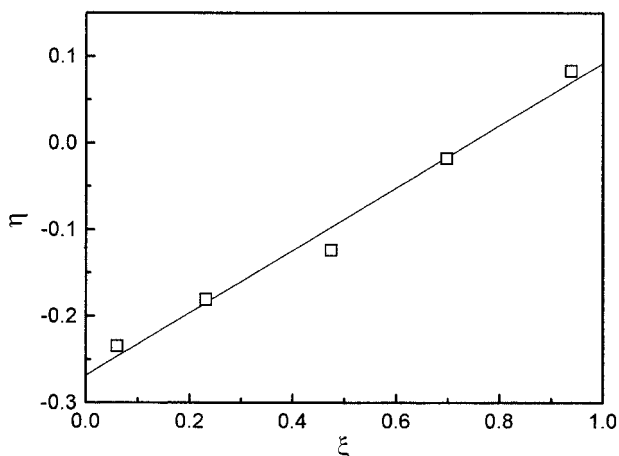
Figure 2 η versus ξ of polymer(AC-co-styrene).

$$\eta = \frac{G}{\alpha + F}$$

$$\xi = \frac{F}{\alpha + F}$$

$$F = \left(\frac{f_1}{f_2}\right)^2 \left(\frac{F_2}{F_1}\right)$$

$$G = \left(\frac{f_1}{f_2}\right)\left(1 - \frac{F_2}{F_1}\right)$$

$$\alpha^2 = F_{min}F_{max}$$

In the Kelen–Tüdös equation

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (2)$$

where

The conventional method allows only a conversion of ~ 5%, but the extended Kelen–Tüdös method provides reliable reactivity ratios up to ~ 60% conversion.[20]

McFarlane and coworkers[17] also suggested that critical experiments should be designed for a previously unreported monomer pair; one should predict reactivity ratios using the Q, e scheme by the Alfrey–Price equation[21] to determine approximately the values of r_1^*, r_2^*, and then use eq. (3) to design the critical experiments.

Table VI Copolymerization of AC (M_1) and Vinyl Acetate (M_2) at 42°C Initiated by DCPD ([Initiator] = 2.84×10^{-2} mol L^{-1})

Run	$[M_1]_0 + [M_2]_0$ (mol L^{-1})	f_1	f_2	Time (h)	Yield (%)	F_1[a]	F_2
1	10.66	0.602	0.398	11	30	0.683	0.317
2	11.01	0.486	0.514	9	48	0.636	0.364
3	10.81	0.346	0.654	9	40	0.578	0.422
4	10.62	0.201	0.799	11	32	0.513	0.487
5	10.97	0.098	0.902	11	25	0.481	0.519

[a] Calculated from polymer(methyl acrylate-co-vinyl acetate) by ^{1}H-NMR.
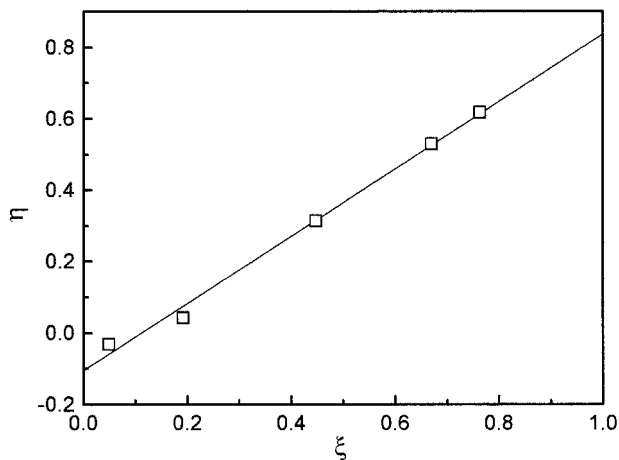
Figure 3 η versus ξ of polymer (AC-*co*-vinyl acetate).

$$f\,'_1 = \frac{2}{2 + r^*_1} \tag{3a}$$

$$f\,''_1 = \frac{r^*_2}{2 + r^*_2} \tag{3b}$$

but the Q and e values from different references are not the same; the critical f_1 calculated with different Q and e values are shown in Table IV (styrene: $Q = 1.00$, $e = -0.80$; vinyl acetate: $Q = 0.026$, $e = -0.88$[22]). According to the results of Table IV, the critical f_1 of AC–styrene ($f\,'_1 = 0.85$, $f\,''_1 = 0.15$) and AC–vinyl acetate ($f\,'_1 = 0.60$, $f\,''_1 = 0.00$) were accepted.

The copolymerization of AC and styrene in dioxane at 42°C with DCPD as initiator is listed in Table V. The η versus ξ plot shown in Figure 2 is linear and r_2 (i.e., r_2/α) and r_1 are obtained from the intercepts at $\xi = 0$ and $\xi = 1$, respectively, computed using the least-squares method. The reactivity ratios r_1 (AC) and r_2 (styrene) were found to be $r_1 = 0.09 \pm 0.1$ and $r_2 = 0.40 \pm 0.1$. The same for AC and vinyl acetate is listed in Table VI and shown in Figure 3, and the reactivity ratios

Table VIII Q and e Values of AC (M_1)

M_2	r_1	r_2	Q	e
Styrene	0.09	0.40	0.58	1.02
Vinyl acetate	0.84	0.03	0.57	1.02
Ref. 24			1.780	1.020
Ref. 23			0.85	1.58
Ref. 22			1.82	1.92
				1.059[a]

[a] Calculated from eq. (4).

r_1 (AC) and r_2 (vinyl acetate) were found to be $r_1 = 0.84 \pm 0.1$ and $r_2 = 0.03 \pm 0.1$.

The critical f_1 calculated with obtained r_1 and r_2 are listed in Table VII.

Results of Table VII show that the accepted critical f_1 in experiments is reasonable.

Determination of Q and e Parameters from r_1 and r_2

The reactivity Q of the monomers and the polarities (e) of their double bond were calculated from the parameters r_1 and r_2 using the Alfrey-Price equation.[21] Another empirical method[25] of determination of e parameters from ^{13}C-NMR data was

$$e(\text{vinyl } X) = \frac{\delta(\text{CH}_2)(\text{ppm/TMS}) - 113.5}{22} \tag{4}$$

the Q_1 and e_1 values of AC from different references are also listed in Table VIII.

From Table VIII, it is obvious that the Q and e values obtained by different methods have some difference, but the Q and e values of us by the Kelen–Tüdös method are the same, and our e values are the same as that of ref. 24 and eq. (4). From the results of our experiments, the Q and e values of AC were 0.58 and 1.02.

Table VII   Critical f_1 Calculated with Obtained r_1 and r_2

	f'_1		f''_1	
	Calculated	Experiment	Calculated	Experiment
AC-St	0.957	0.857	0.167	0.150
AC-VA	0.704	0.602	0.014	0.098

St, styrene; VA, vinyl acetate.

REFERENCES

1. E. Dormann, P. Gruner-Bauer, and P. Strohriegl, *Macromol. Chem., Macromol. Symp.,* **26,** 141 (1989).

2. J. Mort and D. M. Pai, *Photoconductivity and Related Phenomena,* Elsevier, New York, 1976.

3. H. W. Gibson, *Polymer, 25,* 3 (1984).

4. P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymer,* John Wiley & Sons, New York, 1991.

5. S. R. Marder, J. E. Sohn, and G. D. Stucky, *Materials for Nonlinear Optics: Chemical Perspectives,* ACS Symposium Series, Washington, DC, 1991.

6. Y. S. Lipatov, V. V. Tsukruk, and V. V. Shilov, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.,* **C24,** 173 (1984).

7. L. L. Chapoy, *Recent Advances in Liquid Crystalline Polymers,* Applied Science, London, 1985.

8. Y. S. Yang, G. R. Qi, J. W. Qian, and S. L. Yang, Synthesis and hydrolysis study of polyacrylates containing 2′,5-dichloro-4′-nitrosalicylanilide, *J. Appl. Polym. Sci.,* **66,** 29 (1997).

9. H. Müller, O. Nuyken, and P. Strohriegl, *Makromol. Chem.,* **13,** 125 (1992).

10. H. Müller, I. Müller, O. Nuyken, and P. Strohriegl, *Makromol. Chem.,* **13,** 289 (1992).

11. P. Strohriegl, *Makromol. Chem.,* **194,** 363 (1993).

12. H. Staudinger and E. Urech, *Helv. Chim. Acta,* **12,** 1107 (1929).

13. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals,* 3rd ed., Pergamon Press, New York, 1988.

14. Y. X. Qiu, Ph.D. thesis, Zhejiang University, 1992.

15. J. N. Sen, S. R. Chatterjee, and S. R. Palit, *J. Sci. Ind. Res.* (India), **11B,** 90 (1952).

16. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.,* **66,** 1594 (1944).

17. R. C. McFarlane, P. M. Reilly, and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.,* **18,** 251 (1980).

18. T. Kelen and F. Tüdös, *J. Macromol. Sci., Chem.,* **A9,** 1 (1975).

19. F. Tüdös, T. Kelen, T. Földes-Berezsnich, and B. Turcsányi, *J. Macromol. Sci. Chem.,* **A10,** 1513 (1976).

20. T. Kelen, F. Tüdös, B. Turcsányi, and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.,* **15,** 3047 (1977).

21. T. Alfrey and C. C. Price, *J. Polym. Sci.,* **2,** 101 (1947).

22. R. Z. Greenly, *J. Macromol. Sci. Chem.,* **A14,** 427 (1980).

23. Kh. U. Usmanov, Sh. Nadzhimutdinov, and A. S. Turaev, *Dokl. Akad. Nauk SSSR,* **252,** 663 (1980).

24. J. Brandrup and E. H. Immergut, *Polymer Handbook,* 2nd ed., John Wiley & Sons, New York, 1975.

25. J. J. Herman and P. Teyssié, *Macromolecules,* **11,** 839 (1978).