Synthesis, characterization and the reactivity ratios of copolymers of cyclohexyl acrylate with styrene and *N*-vinyl-2-pyrrolidone

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Copolymerization of cyclohexyl acrylate (CHA) with styrene (Sty) and *N*-vinyl-2-pyrrolidone (VPD) was carried out in benzene and dioxane at 70°C and 75°C, respectively, using benzoyl peroxide as initiator. The copolymers were characterized by i.r., ^{1}H n.m.r., g.p.c. and viscometry. The compositions of the copolymers were determined by elemental analysis and the reactivity ratios were computed by Fineman–Ross, Kelen–Tudos and extended Kelen–Tudos methods. $r_{CHA}=0.272\pm0.048$, $r_{Sty}=0.913\pm0.107$ for CHA–Sty system and $r_{CHA}=1.297\pm0.088$, $r_{VPD}=0.122\pm0.014$ for CHA–VPD system are determined by extended Kelen–Tudos method. The *Q* and *e* values for CHA monomer were also determined.

(Keywords: cyclohexyl acrylate; styrene; *N*-vinyl-2-pyrrolidone; copolymerization; characterization; reactivity ratios)

INTRODUCTION

At present, adhesives based on acrylic copolymers are widely used in wood, composite and leather industries because of their versatility and performance characteristics. In the footwear industry, polyurethane adhesives are used for the manufacture of high quality shoes. However, polyurethane adhesives are very expensive and have poor storage stability. In order to find an alternative to this type of adhesive, the development of cyclohexyl acrylate copolymers was undertaken.

To the best of our knowledge, no copolymer systems for the determination of reactivity ratios using cyclohexyl acrylate (CHA) as comonomer have been reported to date. Here our interest is to synthesize and characterize the copolymers of CHA with styrene (Sty) and *N*-vinyl-2-pyrrolidone (VPD), and to determine the monomer reactivity ratios by Fineman–Ross[1], Kelen–Tudos[2], and extended Kelen–Tudos[3] methods.

EXPERIMENTAL

Materials and methods

CHA monomer was prepared by transesterification of cyclohexanol (1 mol) with methyl acrylate (3–4 mol) using concentrated sulfuric acid as catalyst, petroleum ether (50–55°C) as entraining agent and hydroquinone as inhibitor[4].

Styrene (Aldrich) and VPD (Aldrich) were distilled under vacuum before use. Benzene, dioxane and tetrahydrofuran were used after distillation. Benzoyl peroxide (Fluka) was recrystallized from chloroform/methanol mixture.

Copolymerization

CHA–Sty system. Copolymerization of CHA and styrene was carried out in benzene using benzoyl peroxide as initiator under nitrogen atmosphere at 60°C and 75°C. The reaction samples were taken out at regular intervals and precipitated into a large excess of petroleum ether. The percentage yield of the polymer was determined quantitatively (*Table 1*) and the copolymerization reactions were terminated when the conversions reached about 15% (*Table 2*).

CHA–VPD system. Seven copolymers of CHA and VPD were prepared in dioxane using benzoyl peroxide as initiator at 75°C. When conversions reached about 10–20% (120–150 min) the copolymers were precipitated

Table 1 Conversion (%) for copolymerization of CHA–Sty with 2% and 3.3% benzoyl peroxide

	2% Catalyst (60°C) Mole ratio of CHA–Sty in feed		3.3% Catalyst (75°C) Mole ratio of CHA–Sty in feed	
Time (h)	1:9	9:1	1:9	1:1
1	1.28	Trace	13.7	10.02
2	1.80	Trace	20.9	17.50
3	1.97	Trace	34.1	32.10
4	3.73	Trace	41.7	40.00
5	5.03	Trace	–	–

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Table 2 Copolymerization of CHA-Sty (solvent benzene; temperature 70°C; benzoyl peroxide 3.3% based on the monomers weight; monomer/solvent 1.5 (w/v))

Sample no.	Mole fraction of CHA in feed (M_1)	Time (min)	Conversion (wt%)	Elemental analysis (O%)	Mole fraction of CHA in copolymer[a] (m_1)
1	0.30	50	9.11	7.04	0.26
2	0.40	50	5.67	8.97	0.34
3	0.50	60	13.67	10.32	0.40
4	0.60	90	7.18	12.02	0.48
5	0.70	100	12.49	13.20	0.54
6	0.80	100	17.05	15.19	0.65
7	1.00	60	15.06	20.66	0.99

[a] The intensity of aromatic protons (I_a) with that of total protons (I_t) was used for the estimation of copolymer composition using equations (3) and (4) from ^{1}H n.m.r. data:

$$I_a/I_t = 5m_2/(8m_2 + 14m_1) \tag{3}$$

$$m_1 = (5I_t - 8I_a)/(6I_a + 5I_t) \tag{4}$$

where m_1 and m_2 are mole ratios of CHA and Sty in copolymer, respectively

Table 3 Copolymerization of CHA-VPD system (solvent dioxane; temperature 75°C; benzoyl peroxide 3% based on the monomers weight; monomer/solvent 1/5 (w/v))

Sample no.	Mole fraction of CHA in feed (M_1)	Time (min)	Conversion (wt%)	Elemental analysis (N%)	Mole fraction of CHA in copolymer (m_1)
1	0.09	150	12.28	7.68	0.32
2	0.15	120	15.00	6.65	0.49
3	0.22	120	17.66	5.77	0.46
4	0.33	120	21.18	4.62	0.55
5	0.50	150	19.38	3.40	0.66
6	0.62	135	18.21	2.50	0.74
7	0.75	140	17.52	1.70	0.82

using petroleum ether as non-solvent and dried in a vacuum oven at 40°C (*Table 3*).

Characterization

Poly(CHA) and copolymers were characterized by i.r. and ^{1}H n.m.r. spectroscopy. The copolymer compositions were determined by elemental analysis. Molecular weights and viscosity were also determined by g.p.c. and viscometry.

RESULTS AND DISCUSSION

CHA–Sty system

Copolymerization of CHA and styrene was carried out in benzene with 2% and 3.3% benzoyl peroxide as initiator at 60°C and 75°C, respectively. Using 2% catalyst for the copolymerization of 1:9 mole ratio of CHA–Sty, only 5% conversion was reached in 5 h; for 9:1 mole ratio of CHA–Sty, there was no copolymerization at all (*Table 1*). This may be due to the presence of trace amounts of hydroquinone[4].

When the amount of catalyst was increased to 3.3% and at the same time the temperature was raised to 75°C, the conversions were about 40% in 4 h (*Table 1*).

The monomer reactivity ratios of the CHA–Sty were determined by Fineman–Ross (F–R), Kelen–Tudos (K–T) and extended K–T methods. For the determination of reactivity ratios, copolymers with low conversion (< 17%) were prepared at six different feed compositions (*Table 2*) and the compositions of the copolymers were obtained by elemental analysis and ^{1}H n.m.r. spectroscopy. The mole fraction of CHA in feed *versus* that in copolymer is shown in *Figure 1*. There is no azeotropic composition, but there will be some tendency towards alternation. The reactivity ratios determined by F–R, K–T and extended K–T are given in *Table 4*. The values obtained by these three methods agree closely within their 95% confidence limits. Also the δ° values for K–T and extended K–T methods are 0.017 and 0.021; since these are less than 0.1 this suggests that the system is a class I system. Also the Q values, around 0.7, indicate that there is no need for planning of this system.

CHA–VPD system

The copolymers were characterized by i.r. spectroscopy. Peaks were obtained at 1735 and 1640 cm^{-1} due to the ester group of CHA, and amide group of VPD units respectively[5]. The C–H stretching peak of cyclohexyl group was present at 1450 cm^{-1}.

Figure 1 represents the plot of mole fraction of CHA in feed *versus* that in copolymer. The curve indicates that the amount of incorporation of CHA is greater in the copolymer than VPD. There is no azeotropic composition, but alternating tendency will be there.

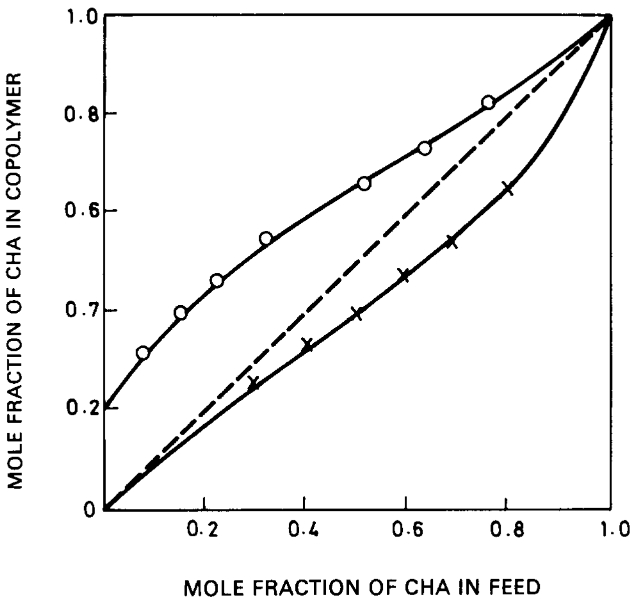

Figure 1 Plot of mole fraction of CHA in feed *versus* mole fraction in copolymer for CHA–Sty system (×) and for CHA–VPD system (○)

Table 4 Comparison of reactivity ratios of CHA–Sty system

Method	r_1(CHA)	r_2(Sty)	$\delta°$	Q	r
F-R	0.317±0.041	0.957±0.169	–	–	0.996
K-T	0.308±0.048	0.933±0.099	0.017	0.701	–
Ex.K-T	0.272±0.048	0.913±0.107	0.021	0.709	–

Table 5 Comparison of reactivity ratios of CHA–VPD system

Method	r_1(CHA)	r_2(VPD)	$\delta°$	Q	r
F-R	1.254±0.055	0.134±0.047	–	–	0.999
K-T	1.256±0.082	0.153±0.017	0.007	0.601	–
Ex.K-T	1.297±0.088	0.122±0.014	0.008	0.589	–

The copolymerization reactivity ratios obtained by F–R, K–T and extended K–T methods for the CHA–VPD system are given in *Table 5*. All values of r_1 and r_2 agree well. The $\delta°$ values for K–T method and extended K–T method are slightly greater than 0.1 but the K–T plots (not shown) suggest that this system is also a class I system. The Q values (0.6) are also good since this system was planned[6].

Q and e values

The Q and e values for the CHA were determined by the Alfrey–Price Q, e scheme[7] using the reactivity ratios obtained experimentally by the K–T method.

$$e_1 = e_2 \pm (\ln r_1 r_2) \qquad (1)$$

A value of $e_2 = -0.8$ was used for styrene.

$$Q_2 = Q_1/r_1 \exp[-e_1(e_1 - e_2)] \qquad (2)$$

The Q and e values for CHA are as follows: CHA–Sty, $e = 0.38$, $Q = 0.43$; CHA–VPD, $e = 0.28$, $Q = 0.19$. The e values obtained from CHA–Sty and CHA–VPD agree well. The Q values differ slightly since equations (1) and (2) give only semi-empirical values. The Q and e values obtained from CHA–Sty were used to determine the r_1 and r_2 values theoretically by using the Alfrey–Price scheme for CHA–VPD; the copolymerization of the CHA–VPD system, could then be planned because VPD is a very low reactive monomer in the copolymerization and comparatively more VPD could be included in the feed compositions.

G.p.c. and viscometry

The weight average molecular weight ($\bar{M}_w$) and the number average molecular weight ($\bar{M}_n$) for CHA–Sty copolymer of 50:50 mol% were obtained by g.p.c. $\bar{M}_w = 13\,899$ and $\bar{M}_n = 9314$. The polydispersity index ($\bar{M}_w/\bar{M}_n$) of 1.5 suggests that termination takes place mainly by recombination[8]. The intrinsic viscosities were also determined by graphical and Solomon–Ciuta methods, giving values of 0.187 and 1.190 dl g^{-1}, respectively. The corresponding [η] values for CHA–VPD copolymer (50:50 mol%) are 0.186 and 0.140 dl g^{-1}.

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