Copolymerization of 2-carboxyphenyl acrylate with styrene and *N*-vinyl-2-pyrrolidone: reactivity ratios, molecular weights and ^{13}C n.m.r. spectra

Manesh D. B. Desai, Boreddy S. R. Reddy, Reza Arshady and Maurice H. George*
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, UK

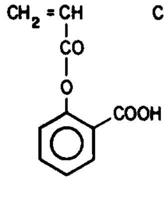
(*Received 7 March 1985; revised 4 July 1985*)

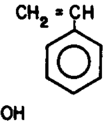
The free radical polymerization of 2-carboxyphenyl acrylate (**1**), styrene (**2a**) and *N*-vinyl-2-pyrrolidone (**2b**), was carried out in the presence of 2,2'-azobisisobutyronitrile, (AIBN), in *N,N*-dimethylformamide solutions at 50°C. Five copolymer samples of **1** and **2a** and seven of **1** and **2b** were prepared under similar conditions and the copolymer compositions were determined by elemental microanalysis. The results were used to calculate the corresponding copolymerization reactivity ratios by both the Fineman–Ross (FR) and Kelen–Tüdos (KT) methods. The reactivity ratios were $r_1 = 0.61 \pm 0.06$, $r_{2a} = 0.49 \pm 0.04$; $r_1 = 0.62 \pm 0.07$, $r_{2b} = 0.00 \pm 0.03$ as determined by the KT method. These values are in good agreement with those determined by the FR method. The molecular weights of the homopolymers were determined by g.p.c. Molecular weights of copolymer samples were also measured by g.p.c. but no simple relationship between copolymer molecular weights and compositions was observed, probably due to the widely differing chemical structures of the samples in each series, and also due to the possibility of chemical transformations in the **1**–**2b** series. ^{13}C n.m.r. spectra of 2-carboxyphenyl acrylate, its homopolymer and its equimolar copolymer with *N*-vinyl-2-pyrrolidone were recorded in $CDCl_3$, and some assignments made from the off-resonance spectra. There was evidence of intra- and intermolecular hydrogen bonding in poly(**1**) and in copoly(**1**–**2a**).

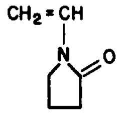
(Keywords: copolymerization; 2-carboxyphenylacrylate; styrene; *N*-vinyl-2-pyrrolidone; ^{13}C n.m.r.)

INTRODUCTION

Polymeric materials carrying the salicylic residue have long attracted attention as potential carriers of aspirin. For example, aspirin derivatives of starch[1] and poly(vinyl alcohol)[2] have been prepared by attachment of salicylic acid by the carboxylic group, or more recently by the phenolic group[3]. The preparation of polymers of methacrylic esters of salicylic acid has also been reported[4]. In an alternative synthetic approach, 5-vinylsalicylic derivatives have been synthesized and (co)polymerized to produce styrene-type aspirin derivatives[5]. Acrylic esters of salicylic acid (2-carboxyphenyl acrylate, or 2-acryloxybenzoic acid, **1** and of methyl salicylate [(2-methoxycarbonyl) phenyl acrylate], are considered to be moderately activated acrylates, and may thus be useful for the preparation of reactive polymers, such as polymer supports or polymeric reagents, by suspension copolymerization[7]. In connection with our own interests in polymeric reagents, we have recently studied the copolymerization, and the copolymers of 2,4,5-trichlorophenyl acrylate with styrene[8], and with *N*-vinyl-2-pyrrolidone[9]. This paper reports the free radical polymerization of **1**, its copolymerization with **2a**, and with **2b**, and the calculation of the corresponding reactivity ratios. The results of gel permeation chromatography, g.p.c. and ^{13}C n.m.r. studies are also described.


1


2a


2b

EXPERIMENTAL

2,2'-azobisisobutyronitrile, AIBN (BDH), was recrystallized from chloroform and dried *in vacuo* at room temperature.

N,N-dimethylformamide, DMF, and diethyl ether (Rose Chemicals, AR), were used as received. Styrene, (BDH), was washed with 5% w/v aqueous sodium hydroxide solution, washed with water, dried over a Linde molecular sieve and distilled under reduced pressure. 2-Hydroxybenzoic acid (BDH), acryloyl chloride (Aldrich Chemicals), quinhydrone and hydroquinone (BDH), were used as received.

N-vinyl-2-pyrrolidone (Aldrich) was purified by fractional distillation under reduced pressure.

Preparation of 2-carboxyphenyl acrylate, 1

2-hydroybenzoic acid (0.4 mole) was stirred in diethyl ether (800 cm^3) at room temperature and triethylamine (0.88 mole) was added over one hour. The solution was

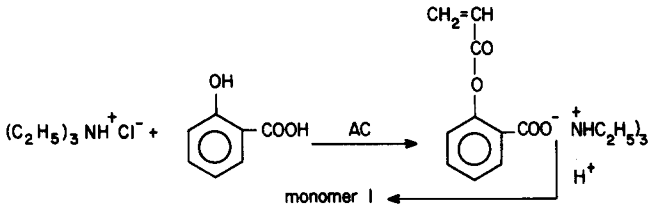
---

[*] To whom all correspondence should be directed.

0032-3861/86/010096-05$03.00

then cooled in an ice-water bath and acryloyl chloride (0.44 mole), AC, in diethyl ether (200 cm^3) was added drop-wise during one hour. The mixture was allowed to stand overnight and solvent was removed under reduced pressure using a Rotavapor. The solid product was dissolved in water, hydroquinone (0.2 g) was added and the solution was acidified with concentrated hydrochloric acid. After cooling, the solid was filtered off and dried in air ($\sim$90% yield). Completion of the reaction was checked by TLC, i.e. ($CHCl_3$:CH_3ON:CH_3COOH, 5:15:10 v/v).

The crude product was crystallized from hot water-2-propanol (1:3 v/v), and dried. (m.pt. 134°C–136°C decomposition)



Polymerization procedures

*Copolymerization of **1** with **2a**.* Appropriate quantities of **1** and **2a** with AIBN and DMF were placed in a standard flask (50 cm^3) and the mixture flushed with oxygen-free nitrogen for at least 10 min. The flask was then tightly stoppered, immersed in a thermostat at 50°C and copolymerization allowed to proceed to about 5–10% conversion (*Table 1*). A small amount of quinhydrone was added to the reaction mixture and DMF was distilled from the reaction mixture at low pressure and low temperature. The solid residue was dissolved in chloroform, methanol or acetone, and precipitated in diethyl ether, in which **1** and **2a** are soluble. The copolymer was reprecipitated, filtered off using a No. 3 sintered glass crucible, and washed repeatedly with fresh diethyl ether to ensure the complete removal of 2-acryloylbenzoic acid and AIBN.

*Copolymerization of **1** with **2b***

Appropriate quantities of **1** and **2b**, with AIBN in DMF, were allowed to copolymerize at 50°C to 5–10% conversion as described above. In general, reaction times were shorter than for the **1**–**2a** system under comparable conditions. At the end of the reaction, copolymerization was terminated by addition of a small quantity of quinhydrone, and DMF was removed at low pressure and temperature. The solid residue was dissolved in chloroform and precipitated into excess diethyl ether. The precipitated copolymer was redissolved in chloroform, reprecipitated as described above and the copolymer filtered off using a No. 3 sintered glass crucible. The solid copolymer was washed repeatedly to ensure the complete removal of 2-acryloylbenzoic acid and AIBN.

Microanalysis. Microanalyses of the copolymer samples were caried out in the Microanalytical Laboratory of this Department. C, H and N contents were measured, as appropriate, and O-contents calculated as necessary. For the system **1**–**2a**, the % oxygen contents enabled mole fractions of **1** to be calculated, while for **1**–**2b**, the %N contents gave the mole fractions of **2b** in the copolymers.

Molecular weight determinations. The weight and number average molecular weights of the copolymers, $\bar{M}_w$ and $\bar{M}_n$, respectively, were determined by gel permeation chromatography (g.p.c.) at the Polymer Supply and Characterization Centre, Shrewsbury, using DMF as eluent, at a flow rate of 1 cm^3 min^{-1}.

^{13}C n.m.r. spectroscopy. ^{13}C n.m.r. spectra were recorded on a WH-250 spectrometer operating at 62.9 MHz in the pulsed Fourier transform mode, with decoupling from protons by broad-band irradiation. The free induction decays were recorded at 16 K, and the chemical shifts (δ) were measured directly relative to Me_4Si.

RESULTS AND DISCUSSION

Copolymerization of 2-carboxyphenyl acrylate, (1), with styrene, (2a), and with N-vinyl-2-pyrrolidone, (2b)

Copolymerizations of **1**–**2a** and **1**–**2b** as well as homopolymerizations of **1**, **2a** and **2b**, were carried out in DMF solution at 50°C in the presence of AIBN. All systems were polymerized to low conversions, usually about 10%. The composition of monomer mixtures, and resulting copolymers obtained by elemental analysis, are summarized in *Tables 1* and *2*, while a plot of the mole fraction of **1** in the monomer feed against the mole fraction **1** in the copolymers for both systems is shown in *Figure 1*. This Figure suggests a strong tendency for alternation for **1**–**2a** with an azeotropic composition at about 50 mole% **1**, whereas the azeotropic composition for **1**–**2b** occurs at a mole% of **1** of about 70.

Copolymerization reactivity ratios

The reactivity ratios of **1**–**2a** and **1**–**2b** systems were estimated by two graphical methods according to Fineman and Ross[10], FR, equation (1), and Kelen and Tüdos[11], KT, equation (2):

$$(F/f)(f-1)=\{r_1(F^2/f)\}-r_2 \tag{1}$$

$$\eta=\{r_1+(r_2/\alpha)\}\zeta-(r_2/\alpha) \tag{2}$$

Table 1 Copolymerization of 2-carboxyphenyl acrylate, **1**, with styrene, **2a**, at 50°C[a]

Mole fraction of **1** in feed	% Conversion	Oxygen content (wt%)	Mole fraction of **1** in copolymer	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
0.0000	2.84	0.00	0.0000	23.02	14.38	1.60
0.1989	9.90	13.52	0.2703	28.82	18.47	1.56
0.3049	6.02	18.07	0.3913	28.36	18.05	1.60
0.4990	8.71	22.13	0.5177	21.36	14.58	1.47
0.6950	5.60	25.88	0.6539	45.69	25.80	1.77
0.7973	7.78	28.42	0.7593	34.40	19.07	1.80
1.0000	9.50	33.30	1.0000	8.82	6.00	1.47

[a] [**1**]+[**2a**]=0.882 mol dm^{-3}, initially, at 50°C; [AIBN]=3.060×10^{-2} mol dm^{-3} at 50°C

F and f are the mole ratios of **1** and **2a** (or **1** and **2b**) in the monomer feed and in the copolymer, respectively. r_1 and r_2 are the reactivity ratios relating to monomer **1** and **2a** (or **2b**), respectively. η, ζ and α are mathematical functions of F and f[9], as defined elsewhere. Typical KT plots are shown in *Figure 2*(i) and *Figure 2*(ii), respectively.

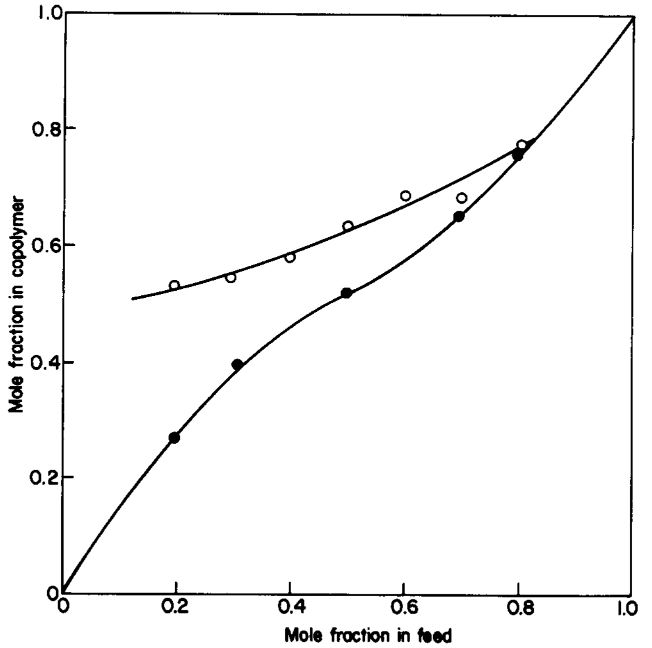


Figure 1 Plot of mole fraction (MF) of monomer **1** in the copolymer against mole fraction in the monomer feed. (●) copolymer system **1–2a**; (○) copolymer system **1–2b**

Least mean squares analysis gave the following results:

$r_1 = 0.64 \pm 0.03$; $r_{2a} = 0.52 \pm 0.07$ by FR method
$r_1 = 0.61 \pm 0.06$; $r_{2a} = 0.49 \pm 0.04$ by KT method
$r_1 = 0.60 \pm 0.03$; $r_{2b} = -0.01 \pm 0.07$ by FR method
$r_1 = 0.62 \pm 0.07$; $r_{2b} = 0.00 \pm 0.03$ by KT method

Bearing in mind the physical significance of reactivity ratios, the method of analysis and the relatively large error involved, the value of r_{2b} is essentially zero. Both FR and KT methods produced reactivity ratios in relatively good agreement.

Gel permeation chromatography (g.p.c.)

The weight and number average molecular weights of homopolymer and copolymers, $\bar{M}_w$ and $\bar{M}_n$, respectively, involving **1** and **2a** were determined by g.p.c. and their values, together with polydispersity indices, $(\bar{M}_w/\bar{M}_n)$, are given in *Table 1*. The fact that $(\bar{M}_w/\bar{M}_n)$ values remain relatively constant at about 1.5, suggests that the bimolecular termination step involving $\sim M_1$ and $\sim M_{2a}$ radicals occurs mainly by combination, which is well established for reaction of two polystyryl radicals[12,13]. However, absolute molecular weight data are required for conclusive interpretation to be made. The corresponding g.p.c. results for the **1–2b** system is given in *Table 2* and all samples showed relatively wide molecular weight distributions, as indicated by their heterodispersity indices. At high concentrations of **2b** in the monomer feeds, above a mole fraction of 0.60, the final g.p.c. trace showed two peaks suggesting that branching had occurred. Since conversions were less than 10%, however, transfer to polymer seems unlikely, and other branching

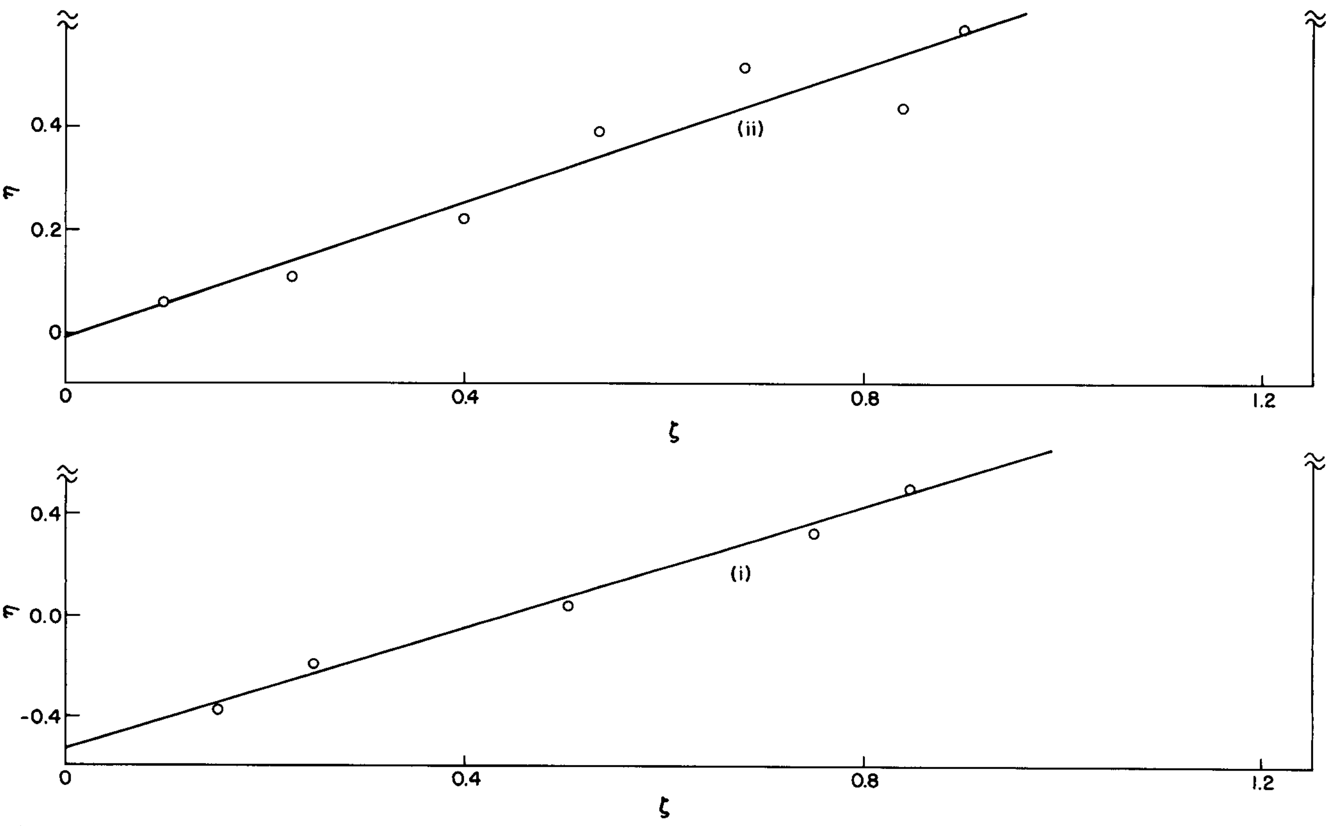


Figure 2 Copolymerization reactivity ratio determinations by the Kelen–Tüdos method. (i) the **1–2a** system; (ii) the **1–2b** system (values of α, equal to $(F_{max} \times F_{min})^{1/2}$, were 0.9033 and 0.5010, for the **1–2a** and **1–2b** copolymerization systems, respectively[9])

Table 2 Copolymerization of 2-carboxyphenyl acrylate, **1**, with *N*-vinyl-2-pyrrolidone, **2b**, at 50°C[a]

Mole fraction of **1** in feed	% Conversion	Nitrogen content (wt%)	Mole fraction of **1** in copolymer	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
0.0000	2.84	12.60	0.000	5.52	1.88	2.94
0.2014	12.56	4.22	0.535	1765	4.74	(double peak)
0.2973	9.48	4.10	0.545	895	30.12	29.71
0.4009	9.94	3.76	0.576	3785	45.54	83.12
0.4997	8.24	3.15	0.634	1970	90.05	21.88
0.6003	10.95	2.69	0.681	1373	48.54	28.28
0.7000	7.03	2.63	0.687	7267	180.71	40.22
0.7981	7.38	1.81	0.775	–	–	–
1.0000	9.50	0.00	1.000	8.82	6.00	1.47

[a] [**1**] + [**2b**] = 0.886 mol dm^{-3}, initially, at 50°C; [AIBN] = 3.049 × 10^{-2} mol dm^{-3} at 50°C

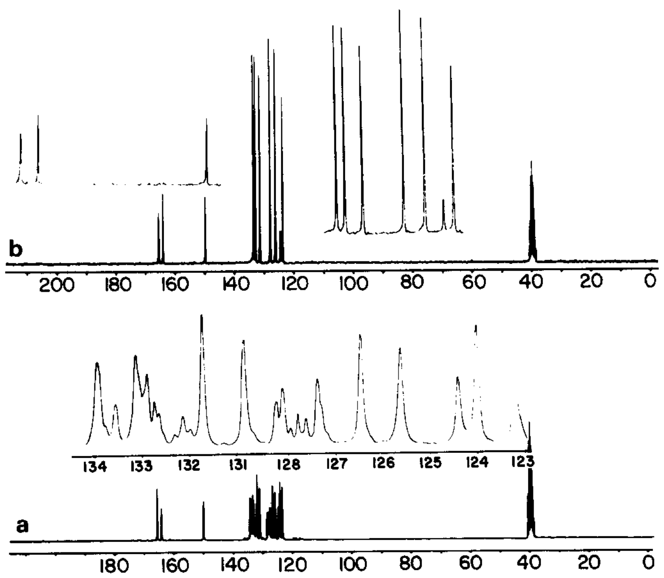


Figure 3 ^{13}C n.m.r. spectra (a) 2-carboxyphenylacrylate, **1**; (b) off-resonance spectrum of **1**

mechanisms, possibly involving the carbonyl functions, may be involved.

^{13}C *n.m.r spectroscopy*

^{13}C n.m.r. spectra of 2-carboxyphenyl acrylate, **1**, its homopolymer, and an equimolar copolymer with *N*-vinyl-2-pyrrolidone, are shown in *Figures 3a*, *4c* and *4b*, respectively. Assignments to various carbons were made from the corresponding off-resonance spectra. The off-resonance spectra of monomer **1** and poly(**1**) are given in *Figures 3b* and *4d*, respectively. Different carbon atoms in the molecule show different line intensities due to differential Overhauser effects and spin-lattice relaxation times. It is interesting that in *Figure 3a* all six carbon atoms in the phenyl ring of **1** are well resolved due to the substitutional effects of the carbonyl and phenoxy-carbonyl groups. The effects of substituents on the resolution of six carbon atoms was reported previously in the case of 2,4,5-trichlorophenyl acrylate monomer[8]. Chemical shift assignments of various carbons are presented in *Table 3*.

The aromatic carbon C^1 is split into two peaks in poly(**1**) as observed in *Figure 4c*. This indicates that C^1 carbon is susceptible to tacticity (iso-, syndio- or hetero-)[14,15]. The ester carbonyl and the carboxyl carbonyl groups in poly(**1**) each gave three and two peaks, respectively, ($\underline{-COO:}$ 163.10, 164.86 and 165.57 ppm; $\underline{-CO-}$OH: 173.39 and 175.06 ppm). Also, from *Figure 4c*, there are nine well resolved peaks (*Table 3*) in addition to

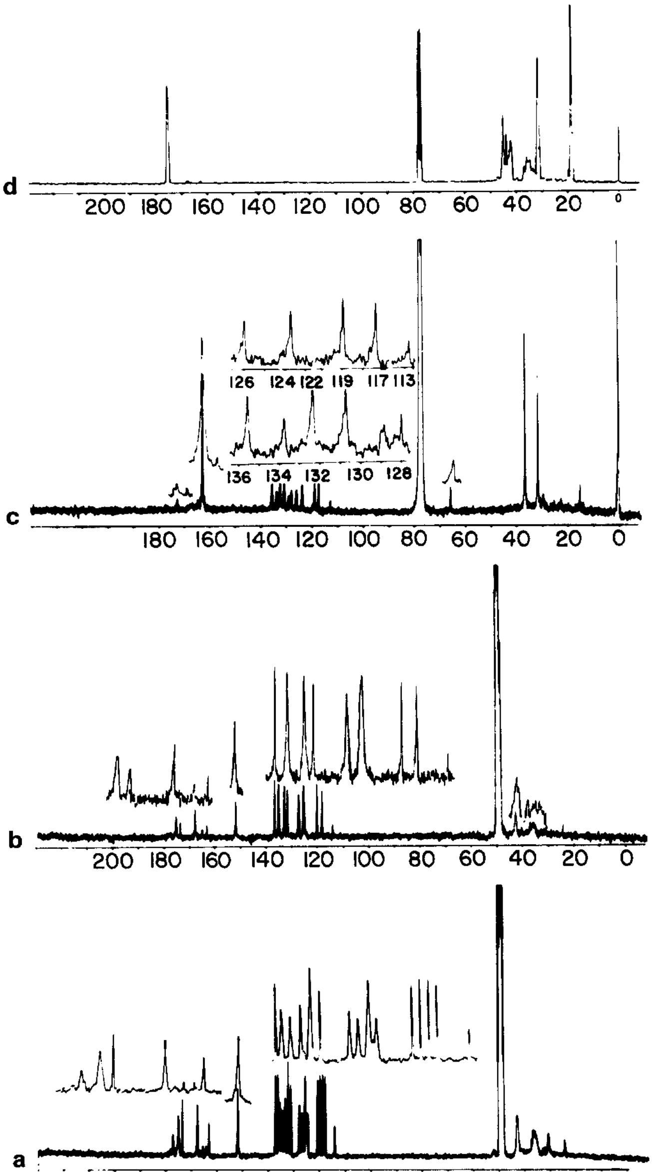
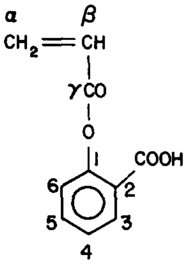


Figure 4 ^{13}C n.m.r. spectra (a) poly(**2b**); (b) copoly(**1**–**2b**); (c) poly(**1**); (d) off-resonance spectrum of poly(**1**)

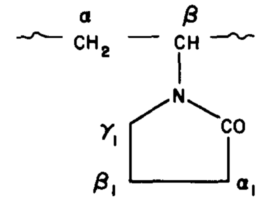
Table 3 ^{13}C n.m.r. chemical shifts[a,b] of 2-carboxyphenyl acrylate, **1**, homo- and copolymers of **1** and **1**–**2b** (*N*-vinyl-2-pyrrolidone), respectively, and poly(**2b**)

	Chemical shifts (δ, ppm)							
Compound	Aromatic ring carbons				C^{α}	C^{β}	CO^{γ}	$\underline{C}O$ OH
1	149.71 (C^1)	124.42 (C^2)	123.56 125.98 } (C^3/C^6)	127.75 133.43 } (C^4/C^5)	132.72	131.21	163.95	162.42
Poly(**1**)	151.75 (C^1)	113.99 118.06 132.66	118.09 120.02 $\Delta\delta = 1.93$[e]	127.13 125.18 $\Delta\delta = 1.95$	42.23 to 43.30 (Broad)	35.23 to 36.98 (Broad)	163.10 164.86 $\Delta\delta = 1.76$	173.39 175.06 $\Delta\delta = 1.67$
Copoly(**1**–**2b**)	162.70 (C^1)[c]	112.78 127.98 128.83 31.53[d] (α_1–CH_2 to CO)	117.34 118.95 $\Delta\delta = 1.61$ 130.68 132.31 $\Delta\delta = 1.63$ 36.51[d] (β_1–CH_2 to CO)	123.71 125.98 $\Delta\delta = 2.27$ 125.98 127.98 $\Delta\delta = 2.00$ 65.82 (γ_1–CH_2 to CO)	36.51[d]	31.53[d]	162.07[c] 163.48 $\Delta\delta = 1.41$ 162.70	172.56
Poly(**2b**)		18.35 (α_1–CH_2 to CO)	18.88 (β_1–CH_2 to CO)	31.46 (γ_1–CH_2 to CO)	41.85 to 43.86 (broad)	34.78 to 36.34 (broad)	175.25	–

[a] cf. structure below
[b] cf. structure below
[c] The peak is broad with three distinct peaks at 162.07–163.48 and is difficult to assign for C^1 and CO^{γ} carbon
[d] The peaks overlap and are difficult to assign
[e] $\Delta\delta$ is the difference in ppm between the peaks



a



b

two peaks as shoulders due to overlapping, at 118.09 and 133.13 ppm, corresponding to the aromatic rings. Also there is symmetry in the separation peaks corresponding to the carbon atoms in the aromatic ring. The differences in the chemical shifts, $\Delta\delta$, were 1.93 and 1.95 ppm in the case of the two sets of peaks at 118.09 (120.02) and 125.18 (127.13), respectively. Similarly, $\Delta\delta$ values were 1.63 and 1.61 for the peaks at 131.50 (133.13) and 134.88 (136.49) ppm, respectively. These additional peaks corresponding to the aromatic ring carbons may be attributed to intra- and intermolecular hydrogen bonding. Hydrogen bonding between –COOH and –C=O adjacent to CH within the same polymer molecule is also possible, but less likely. This type of intramolecular H-bonding was reported earlier[16] between the ester carbonyl and the –NH– group of poly(2-formamido-2-methylpropyl acrylate).

For copoly (**1**–**2b**) the splitting of C^1 carbon was difficult to assign as shown in *Figure 4b*. However, there are eleven well resolved peaks corresponding to the aromatic carbons (*Table 3*), similar to the observations for poly(**1**). The values of $\Delta\delta$ for copoly(**1**–**2b**) were 1.61 and 1.63 ppm for the two sets of peaks at 117.34 (118.95) and 130.68 (132.31) ppm, respectively. Similarly, $\Delta\delta$ values were 2.27 and 2.00 ppm for the other two sets of peaks at 123.71 (125.98) and 125.98 (127.98) ppm, respectively. This suggests that intra- and intermolecular H-bonding also occurs in copoly (**1**–**2b**) although the spectrum is further complicated, possibly by complex formation between the *N*-vinyl-pyrrolidone and carboxylic acid groups[17].

REFERENCES

1 Kratzl, K. and Kaufmann, E. *Monatsh. Chem.* 1961, **92**, 371
2 Krapachev, V. A., Lavient'eva, E. M., Podgorskaya, K. S. and Semenova, T. E. *Vysokomol. Soedin.* 1969, **B11**, 857 (from 'Drug Design', Ed. E. J. Ariens, Vol. 10, Academic Press, London, 1980)
3 Havron, A., Weiner, B. Z. and Zilkha, A. *J. Med. Chem.* 1974, **17**, 770
4 Weiner, B. Z. and Zilkha, A. *Isr. J. Chem.* 1973, **11**, 567
5 Bailey, D., Tirrell, D. and Vogl, O. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2725
6 Arshady, R. *Makromol. Chem., Rapid Commun.* 1981, **2**, 573
7 Arshady, R. and Ledwith, A. *Reactive Polym.* 1983, **1**, 159
8 Reddy, B. S. R., Arshady, R. and George, M. H. *Macromolecules* 1983, **16**, 1813
9 Reddy, B. S. R., Arshady, R. and George, M. H. *Eur. Polym. J.* (submitted for publication)
10 Fineman, M. and Ross, S. D. *J. Polym. Sci. Polym. Chem. Edn.* 1950, **5**, 259
11 Kelen, T. and Tüdos, F. *J. Macromol. Sci., Chem.* 1975, **A9**, 1
12 Bevington, J. C., Melville, H. W. and Taylor, R. P. *J. Polym. Sci.* 1954, **12**, 449
13 Teramachi, S., Hasegawa, A., Akatsuka, M., Yamashita, A. and Takemoto, N. *Macromolecules* 1978, **11**, 1206
14 Inoue, Y., Nishioka, A. and Chujo, R. *Makromol. Chem.* 1972, **156**, 207
15 Shaefer, J. *Macromolecules* 1971, **4**, 107
16 Reddy, B. S. R., Arshady, A. and George, M. H. *Makromol. Chem.* 1984, **185**, 1383
17 Litmanovich, A. A., Papisov, I. M. and Kabanov, V. A. *Eur. Polym. J.* 1981, **17**, 981