Non-classical free-radical polymerization: 5. The purification and polymerization of 1-vinyl-2-pyrrolidone

Clement H. Bamford
Bioengineering and Medical Physics Unit, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

and Edward Schofield and David J. Michael
Research Laboratories, Kodak Limited, Harrow, Middlesex, HA1 4TY, UK

(*Received 23 August 1984*)

The impurities in 1-vinyl-2-pyrrolidone (NVP) have been investigated by g.c./m.s. and ^{13}C n.m.r. The inadequacy of normal purification procedures is pointed out, and a simple technique for reducing the impurity-level to undetectable values is described. Sources of non-ideality in free-radical polymerization are classified and it is suggested that a plot of $\omega\mathscr{I}^{-0.5}$ vs. [M] could be particularly valuable in revealing the origins of non-ideal behaviour, including the presence of retarders. (ω, $\mathscr{I}$ are the rates of polymerization and initiation, respectively, and M represents monomer). Extensive data on NVP polymerization in ethanol solution at 60°C with azo-bis-isobutyronitrile as initiator have been obtained by dilatometric studies; for this purpose redetermination of the polymer density proved necessary. The data have been analysed as outlined above. The efficacy of the purification procedure in removing 'active' impurities has thus been demonstrated and it is concluded that, as already suggested by others, the polymerization under the prevailing conditions is subject to a medium effect operating principally on the propagation process. This is discussed briefly.

(Keywords: purification by zone melting; free-radical polymerization; monomer and polymer densities; non-classical behaviour; kinetic diagnosis; medium effects)

INTRODUCTION

The purification of 1-vinyl-2-pyrrolidone (NVP) is a long-standing problem which becomes of paramount importance when polymerization of the monomer is being studied. In 1957 Breitenbach[1] remarked that the monomer 'is extremely sensitive to impurities during polymerization'; for a highly purified sample he reports that the rate of polymerization initiated by azo-bis-isobutyronitrile at 20°C is 'more than 20 times the rate we found with a monomer which was purified only by fractionation under reduced pressure'. Unfortunately the purification procedure is not described. Karaputadze *et al.*[2] mention conflicting data in the literature on the polymerization of NVP and imply that difficulties of purifying the monomer may be responsible. These authors subjected their monomer to a 'special purification procedure followed by distillation', but give purification procedure followed by distillation', but give no details of the method. The monomers used in the kinetic experiments of Karaputadze *et al.* were stated to be 99.9% pure. Kaplan and Rodriguez[3] reported a determination of the absolute rate coefficients in the polymerization in isopropanol solution and subjected the monomer to crystallization from isopropanol at −25°C. These authors do not report the purity of their monomer or specify the nature of any impurities. Other workers[4–8] appear to have relied on fractional distillation in vacuum for monomer purification.

In the course of kinetic studies of NVP polymerization we encountered problems of non-reproducibility attributable to variations in monomer purity. Generally, rates of polymerization were adequately reproducible for high initiator concentrations but became erratic at low concentrations. We were unable to purify the monomer successfully by partial pre-polymerization. In this paper we describe investigations of the nature and concentrations of impurities in the monomer and give a method of purification which reduces the levels of all impurities to below the limits detectable by g.c.

Measurements of rates of polymerization in ethanol solution at 60°C with azo-bis-isobutyronitrile as initiator are also described, and include data for monomer which we believe to be pure. Rates were generally measured dilatometrically, but a few gravimetric rates were also observed. Since use of the polymer and monomer densities reported by Braun, Disselhoff and Quella[9] led to considerable discrepancies we redetermined these quantities, obtaining a value for the polymer density which differed significantly from that of the earlier workers. Our dilatometric results are based on the new measurements.

EXPERIMENTAL

G.c. observations were performed on a Hewlett–Packard instrument 5880A incorporating a 25 m silica capillary column with a coating of CP wax 57CB as stationary phase.

0032-3861/85/060945–06$03.00

G.c.–m.s. determinations were made with a Finnigan 4600 instrument with a column similar to that mentioned above.

A Jeol FX100 *FT* n.m.r. spectrometer was employed to record ^{13}C n.m.r. spectra.

Densities of monomer and polymer were measured by conventional means with a density bottle and dodecane as a non-swelling liquid for the polymer. Trapped air was removed by many repeated evacuations. The values obtained were 1.007 and 1.197 g cm^{-3} for monomer and polymer, respectively, at 60°C. (The corresponding densities reported by Braun *et al.*[9] were 1.007 and 1.152 g cm^{-3}.)

Polymerizations were followed dilatometrically at (60 ± 0.05)°C. Reaction mixtures were degassed under high vacuum by the conventional freeze–thaw technique. Five cycles were usually sufficient to attain a residual gas pressure $< 10^{-5}$ Torr.

2,2′-azo-bis-isobutyronitrile, ex BDH, was purified by two recrystallizations from methanol. Ethanol A.R., ex James Burroughs, was refluxed for 2 h in the presence of sodium and diethyl phthalate, fractionally distilled and stored under nitrogen.

Monomer purity and purification

Impurities. Acetaldehyde, 1-methylpyrrolidone and 2-pyrrolidone have been found[2] as impurities in NVP by g.c. Samples we obtained from Aldrich and Koch-Light did not contain any of these compounds as major impurities, except 2-pyrrolidone, although other components were found and were common to all samples, irrespective of source and batch number; only the impurity-contents varied. There were even variations in the impurity levels in samples of the same batch number supplied on different dates.

Examination of samples as received by g.c./m.s. revealed two readily discernible impurities, both with a molecular weight of 125, which are thought to be 4-methyl- and 3-methyl-1-vinylpyrrolidone. A third impurity with the same molecular weight, present in much lower concentrations, is only resolvable with difficulty and is believed to be the 5-methyl-isomer.

Evidence for these identifications was obtained from g.c./m.s. and n.m.r. observations as summarized above.

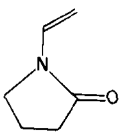
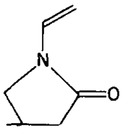
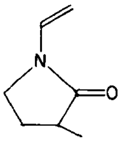
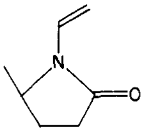
The ^{13}C n.m.r. spectrum was accumulated using the spectrometer in double precision mode (i.e. 32 bit word length). After 60 000 scans on a 5 mm sample a spectrum was obtained which showed six small signals between 20 and 52 ppm. These were not clearly seen in a single precision experiment and are consistent with the presence of the three methyl-1-vinylpyrrolidone isomers as impurities.

The gas chromatogram of a typical sample (99.6% purity) is shown in *Figure 1a*; the major impurities, the methyl-1-vinylpyrrolidone isomers and pyrrolidone, are present in the following quantities (% w/w):

3-MeNVP (3): 0.2
4-MeNVP (4): 0.1
5-MeNVP (5): detectable
pyrrolidone (P): 0.07

Purification. The monomer was first purified with the aid of a simple form of zone-refining. About 200 cm^3 of the sample of *Figure 1a* in a flask were cooled slowly until the monomer froze; the flask was then inverted and the solid allowed to melt slowly at room temperature. Fractions (~ 10 cm^3) were collected as melting proceeded. *Figures 1B, C, D* are gas chromatograms of various fractions and indicate the success of the purification process. The final fraction in this experiment appeared to be effectively pure.

Mass spectral data

Compound	M/Z	Assignment
	111 83 82 68 56 (100%; accurate mass measurement = 56.0495 $\equiv C_3H_6N$)	$M^{+\cdot}$ $(M-CO)^{+\cdot}$ $(M-HCO)^{+\cdot}$ $(M-HCH_2CO)^{+\cdot}$ $(CH_3\text{-}N\text{-}CH{=}CH_2)^{+\cdot}$
	Impurity A (elutes first) 125 82 56 (100%)	 $M^{+\cdot}$ $(M-CH_3CO)^{+\cdot}$ $(CH_3\text{-}N\text{-}CH{=}CH_2)^{+\cdot}$
	Impurity B (elutes second) 125 56 (100%)	 $M^{+\cdot}$ $(CH_3\text{-}N\text{-}CH{=}CH_2)^{+\cdot}$
	Impurity C (elutes third) 125 110 (100%) 70	 $M^{+\cdot}$ $(M-CH_3)^{+\cdot}$ $(CH_3CH_2\text{-}N\text{-}CH{=}CH_2)^{+\cdot}$

The progress of purification and the volume of pure monomer obtainable naturally depend on the rate of crystallization as well as on the purity of the original sample. The first sample is considerably less pure than the original since it concentrates the impurities; as a result it shows the presence of compounds other than the methyl-1-vinylpyrrolidones in concentrations too small to detect in the original (cf. *Figures 1A, B*). In general, the slower the crystallization the greater the proportion of pure monomer obtained. By the simple method described we have recovered over 50% of pure monomer in a single run. If the presence of water is deleterious (we have found it does not influence the polymerization in quantities of a few % w/w) it is necessary to carry out the operations in a dry atmosphere, or to dry the monomer subsequently.

Clearly more elegant forms of zone-refining are applicable. Slow fractional crystallization should also be effective, but we have not explored it in detail.

Polymerization—general

The classical expression (1) for the rate ω of a free-radical polymerization is essentially a gas-phase relation which holds in liquid systems under certain conditions ($\mathscr{I}$ is the rate of initiation, M represents monomer, and k_p, k_t are the velocity coefficients of propagation and bimolecular termination, respectively). Deviations may be classified as follows.

$$\omega = k_p k_t^{-0.5}[M]\mathscr{I}^{0.5} \qquad (1)$$

(i) The initiator exponent 0.5 implies second-order termination between propagating chains, and any process interfering with this may cause deviations from 0.5. Well-recognized examples are primary radical termination

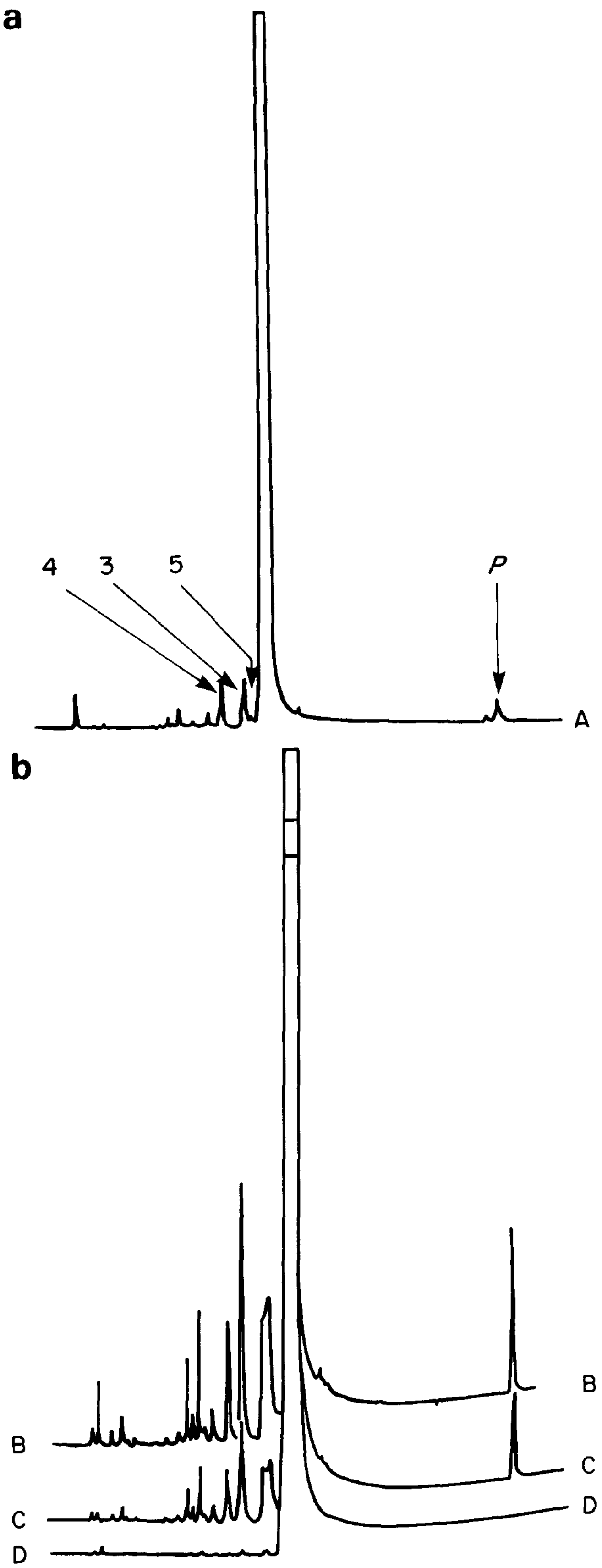


Figure 1 Purification of NVP: gas chromatograms of fractions obtained by freezing and progressive melting as described in text. (a) (A) original sample, (b) (B), (C), later fractions, (D) final fraction. 3(4,5) = 3 – (4 – ,5 –) methyl 1-vinylpyrrolidone. Compositions (%w/w).

	NVP	4-MeNVP	3-MeNVP	5-MeNVP	Pyrrolidone
(A)	99.58	0.11		0.21	0.07
(B)	98.69	0.15		0.51	0.26
(C)	99.45	0.16		0.06	0.17
(D)	99.994	—		—	—

(not, of course, peculiar to polymerization in solution) and degradative chain transfer[10] or addition[11], which give rise to exponents <0.5 and >0.5, respectively. If the termination coefficient k_t is a function of chain-length, relation (1) is likely to be obscured in experiments involving significant changes in average chain-length. A chain-length dependence of k_t has been demonstrated for short chains[12]. Kinetically this feature has resemblances to primary radical termination; thus, both are likely to become important at sufficiently high rates of initiation, or low monomer concentrations.

(ii) Departure from gas-phase conditions may be accompanied by deviations from equation (1). In general, this relation would be expected to break down for monomer–solvent mixtures which are not ideal. More specifically, monomers with ionizable groups are particularly prone to medium influences, but even when no such groups are present phenomena such as monomer–radical and solvent–radical complexing[13,14], hydrogen bonding[2,4,5,15,16], and enolization[17] have been invoked to account for an observed dependence of k_p on composition, leading to deviations from equation (1). Several authors[2,9] have reported the existence of a medium effect in NVP polymerization, manifested by variations in k_p.

The effects of radical occlusion and viscosity on bimolecular termination are well-established. Radical occlusion will not concern us here, but we note that $k_t \propto \eta^{-1}$.

Free- radical initiators in kinetic studies are normally present in low concentrations, so that their concentrations and thermodynamic activities are likely to be effectively equal. In these circumstances rates of initiation are proportional to initiator concentrations. It therefore appeared to us that the quantity $\omega\mathscr{I}^{-0.5}$ could be used more advantageously than higherto in analysing polymerization data. We shall assume that secondary processes such as solvent-induced initiator decomposition are unimportant; when investigating a polymerization it is obviously desirable to choose an initiator free from such complications. For the moment we also assume that medium viscosity is effectively independent of monomer concentration and is therefore not responsible for affecting the rates; this factor is easily examined separately, and we shall refer to it later.

We suggest that a plot of $\omega\mathscr{I}^{-0.5}$ vs. [M] is valuable in demonstrating the origins of non-classical behaviour.

Case A—medium effects insignificant

(Aa) If there are no complications in the termination process, the reaction shows classical behaviour and equation (1) is obeyed, so that the plot of $\omega\mathscr{I}^{-0.5}$ vs. [M] is a single straight line, of slope $k_p k_t^{-0.5}$.

(Ab) When termination is not purely second-order in propagating radical concentration, plots for different values of $\mathscr{I}$ will not coincide and may be curved. Concavity towards the [M]-axis will certainly appear if monomer behaves as a retarder. The common causes of departure from second-order termination in homogeneous systems at low degrees of conversion are retardation and primary radical termination. With most monomers we believe it is possible to locate a range in rates of initiation over which such effects are insignificant. This range is bounded by an upper limit $\mathscr{I}_u$ which is not large enough to cause primary termination or chain-length dependence of k_t to become important (at the appropriate [M]), and a lower limit $\mathscr{I}_l$ which is sufficiently high to eliminate the effect of retarders. This latter may not be practicable if the concentration of retarders is high, or if the monomer itself is a powerful retarder, but such cases do not really concern us here.

If $\mathscr{I}$ lies in the range $\mathscr{I}_u$–$\mathscr{I}_l$, the polymerization follows equation (1) and a linear plot like that in case Aa is obtained.

Case B—medium effects important

(Ba) In the absence of perturbations to the second-order termination, plots for different values of $\mathscr{I}$ will be coincident and non-linear, their shape indicating the form of the dependence of $k_p k_t^{-0.5}$ on the composition of the medium.

(Bb) This is the general case including both medium effects and termination perturbations; it will give rise to plots similar to those in Ab. However, in principle, the two cases are distinguishable since the termination perturbations may usually be effectively eliminated by using values of $\mathscr{I}$ in the range $\mathscr{I}_u$–$\mathscr{I}_l$ defined above. By suitable choice of conditions, linear plots may be obtained in case Ab, but not in the present case, for which the points over the limited range of $\mathscr{I}$ will define a single curve as in case Ba. The approach to a single *curve* with increasing $\mathscr{I}$, as opposed to a straight line, is suggestive of a medium effect.

RESULTS AND DISCUSSION

Data on the polymerization of NVP in ethanol at 60°C with azo-bis-isobutyronitrile as initiator are presented in *Tables 1* and *2*. Values of the rate of initiation have been calculated from the initiator concentration I with the aid of equation (2).

$$\mathscr{I} = 1.3 \times 10^{-5}\,[\mathrm{I}]\ \mathrm{mol\ dm^{-3}\ s^{-1}} \qquad (2)$$

but we must stress that the validity of the discussion does not rest on the numerical accuracy of this relation, and indeed replacement of $\mathscr{I}$ by [I] would not affect the conclusions. However, use of $\mathscr{I}$ allows different initiators to be compared more readily. Rates of polymerization in the Tables refer to initial steady values.

Table 1 presents data for pure NVP; $\omega\mathscr{I}^{-0.5}$ is plotted against [M] in *Figure 2*. The points (20 in number) define, within experimental error, a single curve. Run 385 gives a point lying below the curve; the initiator concentration here, and the rate of initiation, are extremely low so that minute traces of retarders, not detectable by g.c., would be effective. If this point is excluded, the initiator concentrations used in the experiments in *Figure 2* vary over a 14-fold range.

These experiments show that, at constant [M], the rate of initiation may be changed very considerably without causing significant deviation from the curve; thus, in this work $\mathscr{I}$ was situated in the range $\mathscr{I}_u$–$\mathscr{I}_l$ defined earlier. We therefore believe the curve represents the polymerization of pure NVP under our conditions. It is represented moderately closely for $[\mathrm{M}] < 8\ \mathrm{mol\ dm^{-3}}$ by the simple quadratic expression (3).

$$\omega\mathscr{I}^{-0.5} = 0.593[\mathrm{M}] - 0.023[\mathrm{M}]^2\ \mathrm{mol^{0.5}\,dm^{-1.5}\,s^{-0.5}} \qquad (3)$$

Table 2 presents corresponding data for monomer samples which are known to contain impurities of the types mentioned earlier or of which the purity is uncertain (runs 347, 350, 356). The plot of 31 points in *Figure 3* reveals an enormous extent of scatter determined by the different impurity levels and rates of initiation. Clearly in these experiments the rate of initiation does not lie within the range $\mathscr{I}_u$–$\mathscr{I}_l$; mostly $\mathscr{I} < \mathscr{I}_l$. The curve drawn, which is identical with that in *Figure 2*, tends to pass close to points in which a high initiator concentration was used (notably run 262); as mentioned earlier, this condition would minimize the effect of retarders. The greatest deviation from the curve occurs with run 347, with the lowest initiation concentration. There is a tendency in runs at constant $\mathscr{I}$ for the points to deviate increasingly

Table 1 Polymerization of pure NVP in ethanol at 60°C. Initiator: azo-bis-isobutyronitrile

No.	[M] (mol dm^{-3})	10^3 [I] (mol dm^{-3})	$10^9\,\mathscr{I}$ (mol dm^{-3} s^{-1})	$10^5\,\omega$ (mol dm^{-3} s^{-1})	Label in *Figure 2*
92	0.90	0.388	5.044	3.65	●
92	2.26	0.388	5.044	8.37	
92	4.07	0.388	5.044	14.83	
92	6.34	0.388	5.044	18.82	
91	0.90	0.807	10.49	5.81	○
	2.26	0.807	10.49	12.48	
	4.07	0.807	10.49	20.19	
	6.34	0.807	10.49	27.41	
79	0.90	1.544	20.07	6.63	+
	2.26	1.544	20.07	16.00	
	4.07	1.544	20.07	27.43	
	6.34	1.544	20.07	37.55	
382	7.24	0.405	5.25	21.73	△
	7.24	1.579	20.46	44.52	
384	3.60	0.105	1.360	6.86	□
	5.40	0.105	1.360	9.32	
	7.20	0.105	1.360	11.01	
385	6.75	0.0207	0.268	4.16	▲
381	5.40	0.393	5.093	18.49	×
	5.40	1.572	20.373	38.60	

Table 2 Polymerization of impure NVP in ethanol at 60°C. Initiator: azo-bis-isobutyronitrile

No.	Purity of monomer (%)	[M] (mol dm^{-3})	10^3 [I] (mol dm^{-3})	10^9 $\mathscr{I}$ (mol dm^{-3} s^{-1})	10^5 ω (mol dm^{-3} s^{-1})	Label in *Figure 2*
262	98.75	1.35	4.817	62.43	18.90	○
	98.75	2.70	4.817	62.43	36.10	
	98.75	4.05	4.817	62.43	50.11	
	98.75	5.40	4.817	62.43	64.57	
	98.75	7.25	4.817	62.43	71.52	
263	98.75	1.80	1.45	18.79	14.74	●
	98.75	3.60	1.45	18.79	21.64	
	98.75	5.40	1.45	18.79	29.87	
	98.75	7.20	1.45	18.79	33.25	
264	98.75	1.80	0.561	7.27	8.00	■
	98.75	3.60	0.561	7.27	13.26	
	98.75	5.40	0.561	7.27	16.48	
	98.75	7.20	0.561	7.27	18.47	
66	97.70	0.90	1.566	20.30	6.72	△
	97.70	2.25	1.566	20.30	13.74	
	97.70	4.05	1.566	20.30	21.27	
	97.70	6.35	1.566	20.30	25.86	
61	97.70	5.4	1.57	20.35	25.00	▲
	98.70	5.4	1.57	20.35	30.42	
347	unknown	6.34	0.06	0.78	3.43	▼
		6.34	0.05	0.65	2.89	
		6.34	0.04	0.52	2.38	
		6.34	0.02	0.26	1.08	
350	unknown	1.80	1.544	20.01	14.91	×
		5.85	1.544	20.01	34.58	
		8.10	1.544	20.01	37.69	
356	unknown	1.80	0.102	1.33	2.64	□
		3.15	0.102	1.33	4.27	
		4.50	0.102	1.33	5.31	
		5.85	0.102	1.33	6.02	
		8.10	0.102	1.33	6.04	

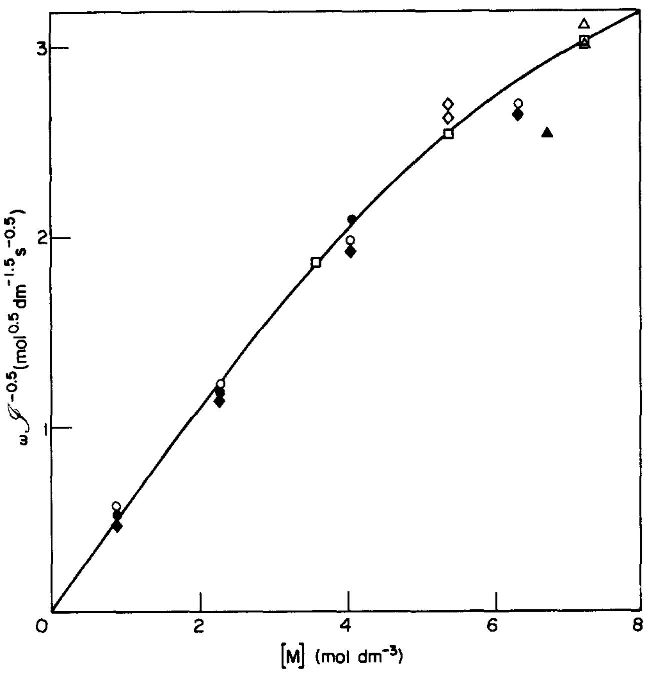


Figure 2 Polymerization of pure NVP in ethanol at 60°C. Initiator: azo-bis-isobutyronitrile. Plot of $\omega\mathscr{I}^{-0.5}$ vs. [M] for data in *Table 1*. Key to points is given in Table

from the curve as [M] increases, consistent with the view that a retarder is present in the monomer.

The curve in *Figures 2* and *3*, which we think represents the polymerization uninfluenced by impurities, and others which may be constructed similarly for different solvents, provide a criterion of purity of the systems.

It seems clear from these results that polymerization of the monomer subjected to conventional methods of fractionation belongs to the general case Bb. After purification by the melting procedure described the monomer polymerizes as in case Ba, the curve in *Figure 2* representing an influence of the reaction medium on the polymerization parameters. The value of $k_p k_t^{-0.5}$ derived from the curve in *Figure 2* by application of equation (1) is shown as a function of [M] in *Figure 4*. As will be seen from equation (3) the parameter decreases monotonically and linearly over the range in [M] studied. *Figure 4* also demonstrates that over the same range the relative viscosity of the reaction medium increases by about 33%, most of the change occurring at relatively high [M]. This would produce an increase in $k_t^{-0.5}$ of approximately 17% (in a sense opposite to that corresponding to the observed decrease in $k_p k_t^{-0.5}$). Most of the medium effect may therefore be exerted on the propagation coefficient, as others have proposed[2,4,5,15,16]. Variations in k_t arising from conformational changes in the propagating chains[4] cannot be excluded on the basis of present information. In

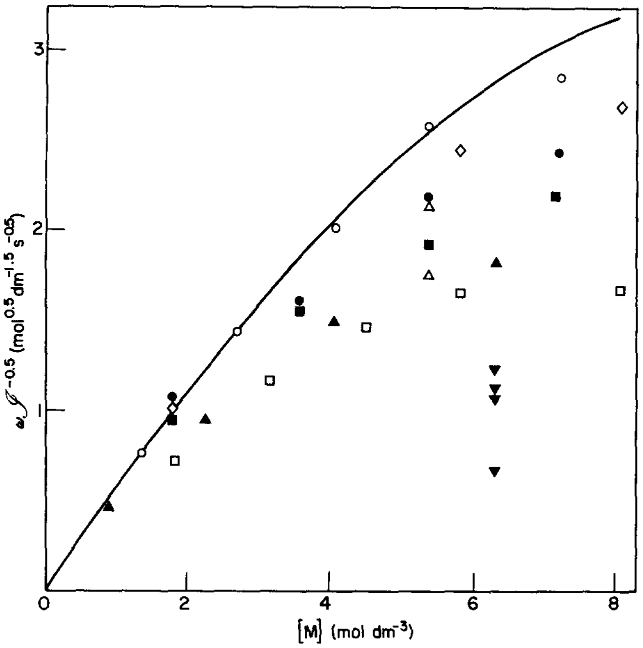


Figure 3 Polymerization of NVP in ethanol at 60°C. Initiator: azo-bis-isobutyronitrile. Plot of $\omega\mathscr{I}^{-0.5}$ vs. [M] for data in *Table 2*, referring to monomer samples subjected to fractional distillation and/or prepolymerization. These processes are inadequate for producing pure monomer as indicated in *Table 2*. Key to points is given in Table

this connection absolute determination of k_p and k_t over a range of compositions would be of interest.

In earlier papers[11] we have discussed the polymerization of *N*-vinylimidazole (VIM) which shows markedly non-classical behaviour in ethanolic solution. We attributed this to degradative addition to monomer and a similar view was subsequently advanced for the photo-initiated reaction by Joshi and Rodriguez[18]. We have confirmed our earlier observations on the purity of our monomer using g.c. conditions identical with those employed in the present work; no impurities of any kind were detectable. The origins of the non-classical behaviour of the two monomers VIM and NVP are different and fall into the categories Ab for VIM and Ba for (pure) NVP. Hydrogen bonding between water and NVP monomer[2,4,5,15,16] or propagating radicals[5] has been suggested as the origin of the relatively high rates of polymerizations in aqueous solution. Kirsh *et al.*[16] have used i.r. and ^{13}C n.m.r. observations to show that hydrogen bonding occurs to the amide group of the NVP molecule in aqueous and ethanolic solutions. This is in accord with expectation, and is consistent with the effective absence of a similar effect from VIM in ethanol, in which weaker hydrogen bonding would be anticipated. In aqueous solutions of VIM we have already reported[11] enhancements of rate arising from monomer–water interactions.

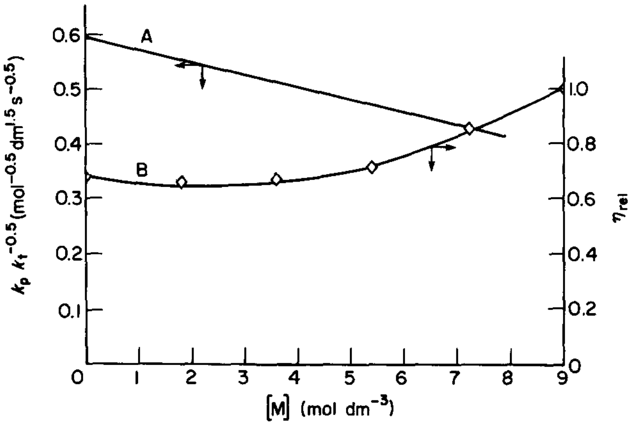


Figure 4 Curve (A): $k_pk_t^{-0.5}$ as a function of [M], derived from *Figure 2*. Curve (B): relative viscosities of NVP–ethanol mixtures at 60°C

ACKNOWLEDGEMENT

The authors are pleased to thank the following members of the Kodak Research Dividion: Dr P. Beynon for carrying out the n.m.r. observations and Messrs A. Payne and J. Trigg for performing the g.c./m.s. analyses.

REFERENCES

1 Breitenbach, J. W. *J. Polym. Sci.* 1957, **23**, 949
2 Karaputadze, T. M., Shumskii, V. I. and Kirsh, Yu. E. *Vysokomol. Soedin.* 1978, **A20**, 1854; *Polym. Sci. USSR* 1978, **20**, 2054
3 Kaplan, R. H. and Rodriguez, F. *Appl. Polym. Symp.* 1975, No. 26, p. 181
4 Senogles, E. and Thomas, R. *J. Polym. Sci. Polym. Symp. Edn.* 1975, **49**, 203
5 Senogles, E. and Thomas, R. A. *J. Polym. Sci. Polym. Lett. Edn.* 1978, **16**, 555
6 Manickam, S. P., Subbaratnam, N. R. and Venkatarao, K. *Makromol. Chem.* 1980, **181**, 2637
7 Van Ekenstein, Alberde, G. O. and Tan, Y. Y. *Eur. Polym. J.* 1981, **178**, 839
8 Van Ekenstein, Alberde, G. O., Koetsier, D. W. and Tan, Y. Y. *Eur. Polym. J.* 1981, **178**, 845
9 Braun, D., Disselhoff, G. and Quella, F. *Makromol. Chem.* 1978, **179**, 1239
10 Atkinson, W. H., Bamford, C. H. and Eastmond, G. C. *Trans. Faraday Soc.* 1970, **66**, 1446
11 Bamford, C. H. and Schofield, E. *Polymer* 1981, **22**, 1227; 1983, **24**, 433; *Polymer* 1983, **24** (*Commun.*), 4
12 O'Driscoll, K. F. *Pure Appl. Chem.* 1981, **53**, 617 and references quoted
13 Henrici-Olivé, G. and Olivé, S. *Makromol. Chem.* 1963, **68**, 219; *Z. Physik. Chem.* 1965, **47**, 286; 1966, **48**, 35, 51; *Makromol. Chem.* 1966, **96**, 1221
14 Bamford, C. H. and Brumby, S. *Pure Appl. Chem.* 1967, **15**, 333; *Chem. Ind.* 1969, 1020
15 Stamm, E. V., Skurlatov, Yu. L., Karaputadze, T. M., Kirsh, Yu. E. and Purmal, A. P. *Vysokomol. Soedin* 1980, **B22.6**, 420
16 Kirsh, Yu. E., Kokorin, A. I., Karaputadze, T. M. and Kazarin, L. A. *Vysokomol. Soedin* 1981, **B23.6**, 444
17 Saini, G., Leoni, A. and Franco, S. *Makromol. Chem.* 1971, **144**, 235; **147**, 213; **146**, 165; 1973, **165**, 97
18 Joshi, M. G. and Rodriguez, F. *J. Appl. Polym. Sci.* 1984, **29**, 1345