Copolymerization behaviour of N,N' — divinylureas

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Copolymerizations of 1,3-divinylimidazolid-2-one (DVI), 1,3-divinylhexahydropyrimid-2-one (DVHHP) and 1-ethyl-3-vinylimidazolid-2-one (EVI) with ethyl acrylate (EA) have been carried out and reactivity ratios determined. For DVI—EA, $r_1 = 0.090$, $r_2 = 0.388$; DVHHP—EA, $r_1 = 0.137$, $r_2 = 0.549$; EVI—EA, $r_1 = 0.094$, $r_2 = 0.530$. The Q and e values for these N-vinylureas have been calculated. 1,3-Diphenyl-1,3-divinylurea inhibits or retards the polymerization of other monomers. The results support the proposal that the N,N'-divinylureas are highly conjugated molecules.

INTRODUCTION

The homopolymerization of a number of N,N'-divinylureas has been reported in earlier papers[1,2]. 1,3-Divinylimidazolid-2-one (DVI) and 1,3-divinylhexahydropyrimid-2-one (DVHHP) gave insoluble crosslinked polymers not cyclopolymers and 1,3-diphenyl-1,3-divinylurea (DPDVU) could not be polymerized under a variety of conditions. These results were attributed to the continuous overlap of π orbitals of the vinyl and carbonyl groups with p_z orbitals on the nitrogen atoms.

As a means of gaining further information on the nature and reactivity of N,N'-divinylureas and the radicals produced from them, a number of copolymerization studies have been carried out.

COPOLYMERIZATION OF N-VINYLUREAS WITH ETHYL ACRYLATE

The copolymer composition equation is used to determine the reactivity ratios and Q and e parameters for the copolymerization of DVI, DVHHP and 1-ethyl-3-vinylimidazolid-2-one (EVI) with ethyl acrylate.

Mixtures of the N-vinylureas and ethyl acrylate in benzene were copolymerized to low conversions using azobisisobutyronitrile as initiator. After precipitation

and purification, the copolymers were analysed for nitrogen content from which the N-vinylurea residues in the copolymer were calculated. Results are summarized in *Table 1*.

Beynon[3,4] investigated the copolymerization of difunctional monomers (diallyl phosphonates and diallylureas) with monofunctional comonomers using the normal form of the copolymerization equation (equation 1). He decided that this equation could be used if the two groups in the difunctional monomer were equivalent, whether or not both functional groups are involved in the polymerization. Thus, for the copolymerization of the N-vinylureas with ethyl acrylate equation (1) (and its derivatives) has been used for the determination of reactivity ratios:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \tag{1}$$

The reactivity ratios were calculated by computer[5] using the method of Fineman and Ross[6] and are given in *Table 2*.

The Q and e values[7] obtained for the N-vinylureas, using values of $Q = 0.52$, $e = 0.22$ for ethyl acrylate, are given in *Table 3*. The values obtained for some other N-vinyl monomers are included for comparison.

The reactivity ratios r_1 and r_2 for the copolymerization of all the N-vinyl monomers studied and ethyl acrylate were both less than one. In such cases there is a strong tendency to form alternating copolymers. The values of r_2 are the reactivity ratios for ethyl acrylate relative to the N-vinyl-

Table 1 Copolymerization of N-vinylureas with ethyl acrylate

Mole fraction EA in feed	Mole fraction EA in copolymer with DVI	Mole fraction EA in copolymer with DVHHP	Mole fraction EA in copolymer with EVI
0.90	0.763	0.842	0.928
0.80	0.720	0.757	0.748
0.70	0.692	0.714	0.662
0.60	0.637	0.687	0.631
0.50	0.640	0.639	0.608
0.40	0.613	0.632	0.568
0.30	0.595	0.597	0.531
0.20	0.592	0.588	0.512
0.10	0.562	0.456	0.519

Table 2 Reactivity ratios for copolymerization of N-vinylureas with ethyl acrylate

System	r_1	r_2
DVI(M_1), EA(M_2)	0.090	0.388
DVHHP(M_1), EA(M_2)	0.137	0.549
EVI(M_1), EA(M_2)	0.094	0.530

Table 3 Q and e parameters for some N-vinyl monomers[a]

Monomer	e	Q
N-vinylurethane	−1.62	0.19
1,3-Divinylimidazolid-2-one[c]	−1.58	0.84
N,N-Divinylaniline	−1.54	0.19
N-ethyl-N-vinylurea	−1.53	0.13
1-Ethyl-3-vinylimidazolid-2-one[c]	−1.53	0.67
N-vinylphthalimide	−1.53	0.36
N-vinylcarbazole[b]	−1.49	0.28
1,3-Divinylhexahydropyrimid-2-one[c]	−1.40	0.68
S-ethyl-N-methyl-N-vinylmonothiocarbamate	−1.29	0.11
N,N-ethylene-N'-vinylurea	−1.19	0.18
N-vinylglycidylurethane	−1.15	0.18
N-vinylpyrrolid-2-one	−1.14	0.14
N-methyl-N-vinyl-p-toluenesulphonamide	−1.10	0.082
N-vinyl-2-oxazolidone	−0.80	0.057
N-vinylsuccinimide	−0.34	0.13

[a] Values taken from ref 8 unless otherwise stated
[b] Ref 9
[c] This work

urea molecules. If the reactivity ratios (R_2) of ethyl acrylate relative to the N-vinyl groups in the N-vinylureas are calculated, we obtain:

ethyl acrylate/1,3-divinylimidazolid-2-one ($R_2 = 2r_2$),
$R_2 = 0.776$

ethyl acrylate/1,3-divinylhexahydropyrimid-2-one
($R_2 = 2r_2$), $R_2 = 1.098$

ethyl acrylate/1-ethyl-3-vinylimidazolid-2-one ($R_2 = r_2$),
$R_2 = 0.530$

Thus, the N-vinyl groups in 1,3-divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one are less reactive than the N-vinyl group in 1-ethyl-3-vinylimidazolid-2-one. This seems to support the proposal of Crawshaw and Jones[1] that a conjugated (resonance stabilized) structure would explain their inability to cyclopolymerize.

The values in Table 3 show that the e values for the new N-vinyl compounds are consistent with other N-vinyl monomers. Since the N-vinyl group will dominate the copolymerization behaviour, and the influence of the various N-substituents will be very similar, it is understandable that the parameter, e, which denotes the polar properties of the monomers and their radicals, will be similar for this series of compounds.

The Q values for the new monomers are much higher than those for the other monomers. However, since the Q–e scheme is an empirical method of analysis, the parameters of which are susceptible only to a quasi-theoretical interpretation, it would be extending the significance of the scheme to attach fundamental importance to these high results.

ATTEMPTED COPOLYMERIZATIONS OF 1,3-DIPHENYL-1,3-DIVINYLUREA

It has already been noted that 1,3-diphenyl-1,3-divinylurea (DPDVU) could not be polymerized by free radical initiators under various conditions, and this was attributed to resonance stabilization of the free radical derived from this monomer[2].

To characterize the polymerization behaviour of DPDVU further, copolymerizations were attempted with certain comonomers. 50% w/w mixtures of DPDVU with vinyl

acetate, ethyl acrylate, methyl acrylate or acrylic anhydride were heated in the presence of 2–3% of initiator (azobisisobutyronitrile) under conditions under which the comonomer alone was shown to be polymerized to high conversion; from none of these mixtures could any (co)polymer be isolated. When styrene was examined as comonomer its polymerization in benzene solution, initiated by azobisisobutyronitrile, was found to be retarded by DPDVU; the product appears to be a copolymer. The rate of copolymerization declines and the DPDVU content of the copolymer increases as the proportion of DPDVU in the comonomer mixture is increased (Table 4). This retardation by DPDVU was observed also in a dilatometric study of the thermally initiated polymerization of styrene alone and with DPDVU (5%) in benzene solution.

DPDVU (50% w/w) was also found to inhibit the polymerization of DVI or DVHHP using 1–5 mol % di-t-butyl peroxide as initiator at 150°C for periods up to 10 h. With 101 mol % initiator (based on DPDVU), during 4.5 h at 150°C glassy polymers were obtained with both comonomers. The infra-red spectra of the latter (after extraction with ethanol) were found to be almost identical to those of poly(1,3-divinylimidazolid-2-one) or poly(1,3-divinylhexahydropyrimid-2-one) respectively.

The results of these copolymerization studies are consistent with the radical derived from DPDVU being rather unreactive; this may be ascribable to resonance stabilization.

EXPERIMENTAL

Purification of monomers and solvents for copolymerization

1,3-Divinylimidazolid-2-one and 1,3-divinylhexahydropyrimid-2-one were crystallized twice from light petroleum ether (b.p. 40–60°C) (analytical reagent) dried at reduced pressure and stored at −5°C.

1-Ethyl-3-vinylimidazolid-2-one was distilled through a Nester–Faust spinning band distillation column equipped with an 18 in stainless-steel band and partial take off head, b.p. 110°C at 1.0 mmHg and stored at −5°C. Ethyl acrylate (mid.cut) was redistilled through a 30 cm column packed with glass helices equipped with a partial take off head (reflux ratio 3:1) b.p. 98.8–99.0°C and stored at −5°C.

Benzene (analytical reagent) was redistilled, b.p. 80.5°C.

Azobisisobutyronitrile was crystallized twice from methanol (analytical reagent) dried over phosphorus pentoxide under reduced pressure and stored at −5°C.

Table 4 Attempted copolymerization of 1,3-diphenyl-1,3-divinylurea with styrene[a]

Feed		Copolymer		
DPDVU (%)	Styrene (%)	Conversion[b]	DPDVU[c] in polymer (wt %)	Reduced[d] viscosity
0.0	100.00	22	0.0	0.256
5.0	95.0	20	1.5	0.228
10.0	90.0	18	2.3	0.166
20.0	80.0	16	2.7	0.124
30.0	70.0	14	3.5	0.109

[a] Polymerized at 50% w/w monomer concentration in benzene with 0.5% w/w azobisisobutyronitrile as initiator for 5 h at 70°C
[b] Estimated gravimetrically by precipitation in methanol
[c] Calculated from nitrogen analysis
[d] Determined in toluene

Copolymerization of 1,3-divinylimidazolid-2-one, 1,3-divinylhexahydropyrimid-2-one or 1-ethyl-3-vinylimidazolid-2-one with ethyl acrylate

Vinylurea monomer and ethyl acrylate (total weight 2.000 g) were weighed into stoppered bottles and transferred using two aliquots of benzene (5 ml each) to polymer tubes containing azobisisobutyronitrile (0.13 mol %). The contents of each polymer tube were made up to 20.0 g with benzene, purged with dry nitrogen and sealed with a rubber serum cap. The tubes were vigorously agitated and placed in a thermostated water bath at $60° \pm 0.1°C$. When the reaction was judged to have proceeded to a few per cent conversion the contents of the tube were slowly poured into vigorously stirred light petroleum ether (b.p. $40-60°C$) (200 ml). The precipitate was collected by filtration, washed repeatedly with light petroleum ether and dried at $55°C$ and 0.1 mmHg for 6 h. The polymers were ground to a fine powder, washed repeatedly with light petroleum ether and dried at $55°C$ and 0.1 mmHg for 24 h. The nitrogen content of the copolymer gave the percentage of vinylurea in the copolymer.

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