necessary for ternary systems in which there is preferential adsorption of one component by another, and that the Casassa theory is at present the most successful in predicting the value of A_2 when solvent–polymer interaction is not too strong.

J. M. G. COWIE

Department of Chemistry,
  University of Essex,
    Wivenhoe Park,
      Colchester, Essex.

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The Free Radical Copolymerization

of N-*Vinyl Carbazole*

N-VINYL carbazole is an interesting monomer for copolymerization studies since it is a powerful charge transfer donor capable of forming complexes with electrophilic species. Indeed in the presence of charge transfer acceptors the free radical polymerization of *N*-vinyl carbazole becomes converted to a cationic process[1]. Such a reaction immediately casts doubt[1] as to whether *N*-vinyl carbazole can copolymerize with weakly electron-accepting comonomers (such as acrylates and methacrylates) by a truly free radical process. However, an analysis[2] of the products of such polymerizations showed that this could be achieved in solution in tetrahydrofuran at 30°C. We report here the reactivity ratios for a series of free radical copolymerizations involving *N*-vinyl carbazole.

All copolymerizations were carried out at 30°C with appropriate amounts of both monomers (total monomer concentration 3·0 moles/litre) and either azo-bis(isobutyronitrile) (10^{-2} moles/litre) or ditertiary butyl peroxide (10^{-2} moles/litre) dissolved in tetrahydrofuran. The polymerizations were continued until conversion of the more reactive monomer reached five to ten per cent, which was usually less than one per cent conversion of the total monomer. Copolymer compositions were determined using elemental analysis. Spectroscopic analysis of the copolymers proved unreliable since the extinction of the carbazole group (the most prominent spectral feature in the u.v. spectrum) was a function of copolymer composition. Copolymer compositions were determined from duplicate runs at four initial monomer feed compositions. The reactivity ratios, r_1 and r_2, and the uncertainties in these values, δr_1 and δr_2, are listed in *Table 1*, where monomer 1 is always *N*-vinyl carbazole.

Table 1. Copolymerization reactivity ratios

Monomer 2	r_1	δr_1	r_2	δr_2	$r_1 r_2$
Cyanoacetylene	0·075	0·005	0·030	0·005	0·002
Acrylonitrile	0·04	0·02	0·28	0·02	0·012
Methyl acrylate	0·11	0·02	0·43	0·02	0·05
p-Chlorostyrene	0·023	0·003	7·0	0·2	0·16
Methyl methacrylate	0·07	0·01	2·7	0·1	0·19
Vinyl acetate	3·9	0·2	0·13	0·03	0·51

It can be seen from the decrease in the product $r_1 r_2$ that the tendency to alternation in the copolymers increases in the series vinyl acetate to cyanoacetylene, as does the general electrophilicity of the comonomer. Although the most strongly electron-accepting comonomers show the strongest tendency towards the formation of alternating copolymers, the reactivity ratios obtained with acrylonitrile, methyl acrylate, methyl methacrylate and vinyl acetate all fit into conventional copolymerization theory. For example, they yield self-consistent Q, e values[3,4] of $+0\cdot43 \pm 0\cdot05$ and $-1\cdot03 \pm 0\cdot1$ respectively. There are no literature values at 30°C, though estimates at temperatures above 65°C give for Q, $0\cdot33^5$, $0\cdot30^6$, $0\cdot41^4$, and for $e-1\cdot60^5$, $-1\cdot20^6$ and $-1\cdot40^4$. Because of the increasing probability of charge transfer initiation at the higher temperatures, it is felt that the values at 30°C are the most reliable.

Using the values of Q and e, values for cyanoacetylene were determined as $Q = +0\cdot163$, $e = +1\cdot43$.

A. M. NORTH and
K. E. WHITELOCK*

Department of Pure and Applied Chemistry,
University of Strathclyde,
Glasgow, C.1.

(*Received April 1968*)

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*Present address: Pilkington Bros., Lathom, Lancs.

Polypropylene Oxide. Rotating Frame Proton Spin–Lattice Relaxation Measurements

MEASUREMENTS of nuclear spin–lattice relaxation times and broad line nuclear resonance spectra are familiar and much exploited techniques for investigating the molecular motions, phase changes and morphology of