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Copolymerization Kinetics of Vinyl Chloride and Vinylidene Chloride in *N*-Methylpyrrolidone Solution

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ABSTRACT: Rates of vinyl chloride–vinylidene chloride copolymerization initiated by AIBN in homogeneous *N*-methylpyrrolidone solution were measured dilatometrically at 50 °C. The minimum in rate at intermediate compositions is far shallower than for systems in which the copolymer precipitates on formation. The results indicate that the rate constant for the termination step does not vary greatly with composition.

In the foregoing paper[1] the kinetics of thermal and photochemical free-radical polymerization of vinylidene chloride (VDC) in homogeneous *N*-methylpyrrolidone solution were reported. It was found that the rate constants and their temperature coefficients were quite normal, in contradistinction to earlier results obtained in heterogeneous systems. Here we describe some copolymerization rate measurements in the same solvent at 50 °C for mixtures of VDC with vinyl chloride (VC).

The VDC–VC copolymerization is of course of considerable practical importance, and has therefore received much attention.[2] Reactivity ratios have been measured several times.[3,4] Rate studies have been published for bulk copolymerization at 45 °C by Reinhardt[5] and at 47 °C by Bengough and Norrish[6] and for both bulk and emulsion copolymerization at 40 °C by Staudinger.[7] The outstanding feature of all these results is the relatively slow rate at intermediate compositions as compared to the rates of homopolymerization of the separate monomers. As remarked by Melville and Valentine,[8] a large relative rate of termination between unlike radicals is required to account for the results. We find less extreme behavior in the homogeneous system.

Experimental Section

Vinylidene chloride, AIBN, and *N*-methylpyrrolidone were purified as before.[1] Vinyl chloride (Matheson Gas Products) was distilled from the tank into a calibrated glass tube and then transferred to the dilatometer,[1] which was immersed in liquid nitrogen. Rate measurements were made as for the homopolymerization of vinylidene chloride, all at 50 °C controlled to within 0.01 °C.

Results

To facilitate analysis, all the measurements of the rate were made as closely as possible at the same initial concentration of AIBN (0.010 mol dm^{-3}) and at the same initial total monomer concentration (2.88 mol dm^{-3}). As before, polymerization was observed to only about 1% conversion and thus the reported copolymerization rates R_p are initial values. The results are given in Table I and displayed graphically in Figure 1. They are again shown as relative rates (based on the homopolymerization of vinylidene chloride) in Figure 2 to permit comparison with the data of Reinhardt[5] and of Staudinger[7] in heterogeneous systems. The differences among these sets of observations emphasize the strong influence of phase conditions on the radical termination step in both homopolymerization and copolymerization.

Discussion

Two different procedures have been used to analyze the results. The classical method is based on the presumption that the reactivity of a radical in both propagation and termination depends only on the identity of the terminal monomer unit and leads to the familiar equation[9–11]

$$R_p \equiv -\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])/\mathrm{d}t$$
$$= \frac{R_i^{1/2}(r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2)}{(r_1^2\delta_1^2[\mathrm{M}_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2[\mathrm{M}_1][\mathrm{M}_2] + r_2^2\delta_2^2[\mathrm{M}_2]^2)^{1/2}} \qquad (1)$$

with $\delta_1 = k_{t11}^{1/2}/k_{p11}$, $\delta_2 = k_{t22}^{1/2}/k_{p22}$, $\phi = k_{t12}/(k_{t11}k_{t22})^{1/2}$. In these expressions, R_i is the rate of initiation, the monomer concentrations are $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$, r_1 and r_2 are the usual reactivity ratios, and the k_{pij} and k_{tij} are propagation and termination rate constants.

For a series of experiments all conducted at a constant value of R_i and a constant value of $[\mathrm{M}_1] + [\mathrm{M}_2]$, the above relation may be rewritten as follows:

$$R_p = \frac{(r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2)}{(r_1^2 f_1^2 R_{p1}^{-2} + 2\phi r_1 r_2 f_1 f_2 R_{p1}^{-1} R_{p2}^{-1} + r_2^2 f_2^2 R_{p2}^{-2})^{1/2}} \qquad (2)$$

where we have put $f_2 = 1 - f_1 = [\mathrm{M}_2]/[\mathrm{M}]$, with $[\mathrm{M}] \equiv [\mathrm{M}_1] + [\mathrm{M}_2]$, and where R_{p1}, R_{p2} represent the rates of homopolymerization at the given values of R_i and $[\mathrm{M}]$, namely

$$R_1 = R_i^{1/2}[\mathrm{M}]/\delta_1, \qquad R_{p2} = R_i^{1/2}[\mathrm{M}]/\delta_2 \qquad (3)$$

Since our experiments were all made at constant values of R_i and of [M], and since the reactivity ratios for the system are well known, the only unknown parameter in eq 2 is the cross-termination rate ratio ϕ. It is well known that there are some implicit assumptions in eq 1 or eq 2, for example, that initiation efficiency and the influence of other possible secondary reactions are independent of composition, and that penultimate influences on reactivity[12] can be ignored.

In Figure 1 curves based on eq 2 are drawn for several constant values of ϕ. With VC as monomer 1 and VDC as monomer **2**, we use $r_1 = 0.22$ and $r_2 = 3.8$, these being chosen as a weighted consensus of the published values.[3,4] It is seen that the data in *N*-methylpyrrolidone solution are best reproduced if ϕ is about 2. This result is consistent with the argument of Melville and Valentine,[8] who obtained the expression

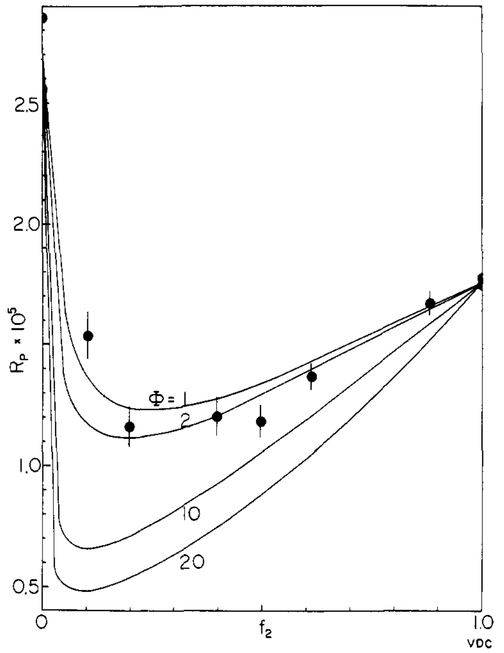

Figure 1. Copolymerization rate at 50 °C (points, Table I) as a function of monomer feed composition (mole fraction f_2 of vinylidene chloride). Curves according to eq 2 for various ϕ values with $r_1 = 0.22$, $r_2 = 3.8$.

Table I
Copolymerization Rates of Vinyl Chloride (1) and Vinylidene Chloride (2) in *N*-Methylpyrrolidone at 50 °C[a]

Mol fraction of 2 (f_2)	10^5R_p, mol dm^{-3} s^{-1}	Mol fraction of 2 (f_2)	10^5R_p, mol dm^{-3} s^{-1}
0	2.56, 2.88	0.495	1.18
0.104	1.53	0.612	1.37
0.201	1.16	0.880	1.67
0.397	1.20	1.00	1.76, 1.77

[a] [I] = 0.010 mol dm^{-3} AIBN. [M] = [M$_1$] + [M$_2$] = 2.88 mol dm^{-3}.

$$\phi^2 = A_{t12}^2/A_{t11}A_{t22}r_1r_2 \tag{4}$$

on the basis of the Alfrey–Price[13] Q–e scheme, the A_{tij} being the frequency factors of the termination rate constants. Since r_1r_2 is near unity for the VC–VDC system, a value of ϕ near unity is expected barring unusual differences among the frequency factors.

If the effects of penultimate units on radical reactivity are considered, ϕ is predicted[44,15] to vary with composition. Our measurements are not sufficiently numerous or precise to justify use of these refinements here.

The second method of analysis is due to Atherton and North[16,17] and is based on the now well established fact that the radical–radical termination reaction is usually diffusion controlled. The rate constant for this process then depends on the over-all composition of the radicals and not specifically on their terminal monomer units. The corresponding rate expression is[16,17]

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{1/2}}{k_t^{1/2}(r_1[M_1]k_{p11}^{-1} + r_2[M_2]k_{p22}^{-1})} \tag{5}$$

where k_t represents the diffusion-controlled termination rate constant, dependent on composition in a way as yet unspecified. As before, we can rewrite eq 5 as

$$R_p = \frac{(r_1f_1^2 + 2f_1f_2 + r_2f_2^2)}{k_t^{1/2}(r_1f_1R_{p1}^{-1}k_{t11}^{-1/2} + r_2f_2R_{p2}^{-1}k_{t22}^{-1/2})} \tag{6}$$

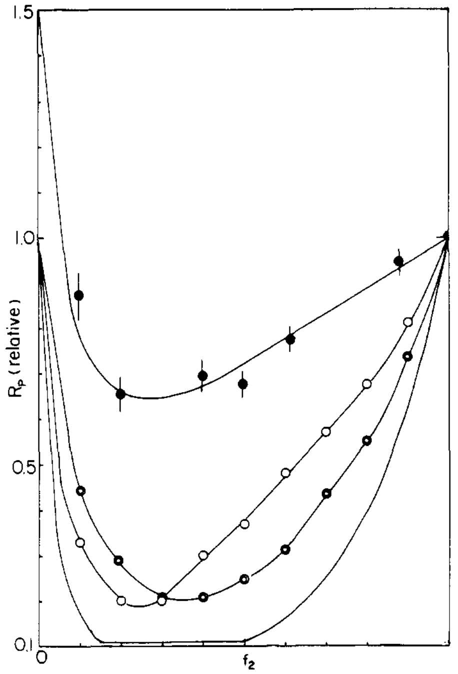

Figure 2. Relative copolymerization rates as functions of monomer feed composition. Filled circles, in homogeneous *N*-methylpyrrolidone solution at 50 °C (Table I); open circles, bulk polymerization at 40 °C (ref 7); concentric circles, emulsion polymerization at 40 °C (ref 7); lowest curve, bulk polymerization at 45 °C (ref 5).

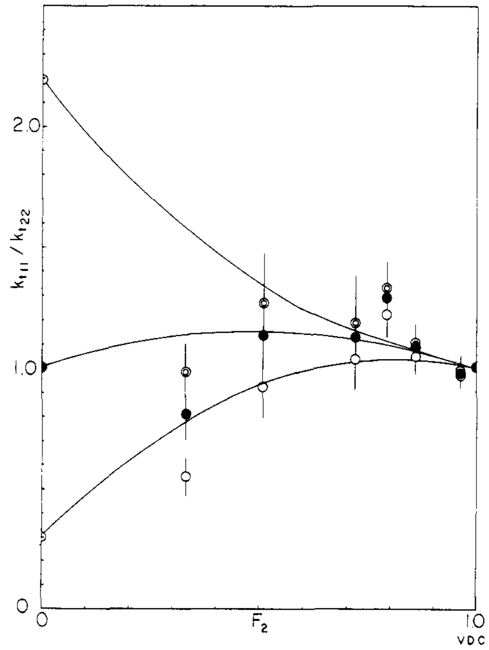

Figure 3. Radical termination rate constant k_t (relative to termination constant k_{t22} for vinylidene chloride) as a function of radical composition F_2, according to the Atherton–North diffusion-control scheme of eq 5–7. Points and curves, from top to bottom, are for assumed ratios k_{t11}/k_{t22} equal to 2.2, 1, and 0.3.

or less symmetrically as

$$R_p/R_{p2} = \frac{(r_1f_1^2 + 2f_1f_2 + r_2f_2^2)}{(k_t/k_{t22})^{1/2}(r_1f_1R_{p2}R_{p1}^{-1}k_{t22}^{1/2}k_{t11}^{-1/2} + r_2f_2)} \tag{7}$$

The last form shows that for any chosen value of the ratio k_{t11}/k_{t22} the data can be inverted to find (k_t/k_{t22}) for each rate experiment. In Figure 3 we show the results of this calculation for several different values of k_{t11}/k_{t22}, plotting k_t/k_{t22} against the mole fraction F_2 of VDC in the copolymer radicals; the latter quantity is given by the standard relation[11]

$$F_2 = (f_1f_2 + r_2f_2^2)/(r_1f_1^2 + 2f_1f_2 + r_2f_2^2) \qquad (8)$$

The three sets of points and curves correspond to chosen ratios k_{t11}/k_{t22} equal to 2.2, 1, and 0.3. The largest of these is obtained by combining the observed k_{t11} of Burnett and Wright[18] for VC in tetrahydrofuran with our own[1] k_{t22} for VDC and correcting (as required by diffusion control[19]) by the ratio $\eta_1/\eta_2 = 0.25$ of the solvent viscosities.[20] It is seen in Figure 3 that smooth curves for k_t as a function of radical composition can be drawn if the point of lowest VDC content is ignored.

We conclude that an adequate description of the system can be based on the Atherton–North treatment, or equally well on the classical one. Our principal result is that there is no anomalous termination behavior in the homogeneous VC–VDC copolymerization system.

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(20) Our observed ratio of homopolymerization rates (Figure 1) is $R_{p1}/R_{p2} \simeq 1.6$, while the combination of Burnett and Wright's data[18] at 50 °C with ours leads to $\delta_1/\delta_2 = 5.3$. Allowance for the viscosity effect on the termination rate ratio, as before, gives $\delta_1(\text{corr})/\delta_2 = 2.6$, in better though not complete accord with R_{p1}/R_{p2}. The remaining effect could be due to a difference in initiation efficiency or to several other possible causes, as mentioned earlier.

Density of Hydrogen Bonds in H-Bond Dominated Solids

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ABSTRACT: Hydrogen-bond dominated solids belong to the class of solids the elastic properties of which, either in theoretical analysis or experimental studies, are found to be related in the first approximation to the density and characteristics of the hydrogen bond with only minor or negligible contributions from covalent, ionic, or van der Waals' bonds or from entropic changes. For such solids, previous work determined that $E = kN^{1/3}$ where E is Young's modulus in dyn/cm^2, N is the number of H bonds per cm^3 effectively carrying the load, and k is a constant equal to 7.8×10^3 dyn/cm for OH- - -O bonds occurring in cellulosics based on H-bond dissociation energy of 4.5 kcal/mol, internuclear distance of 2.7 Å, and a Morse function for the bond potential. In this paper, the value of k is determined from an independent source. By using calculations carried out by Dr. Richard E. Mark and his colleagues at Syracuse University for the three moduli of elasticity for cellulose crystallites, k was calculated for a sheet of randomly oriented crystallites and was found to be $(9.7 \pm 1.6) \times 10^3$ dyn/cm. It is concluded that k probably equals 8.7×10^3 dyn/cm, with an uncertainty of approximately 20%.

The elastic properties of solids are, ultimately, manifestations of changes in their molecular free energies brought about by deformation. Thus, Young's modulus E is in principle calculable from changes in the internal energy and entropy of the solid. In general, the elastic properties of all solids must have contributions from all factors which affect the internal energy and entropy of the system when the solids are deformed. However, it often happens that one contribution predominates to such an extent that, to a first approximation, it alone needs to be considered and others may be neglected. For example, although contributions from the energy potentials of covalent, ionic, and dispersion bonds as well as from the entropy of conformation may generally affect the elastic response of actual samples of natural rubber, very useful predictive formulations of elastomeric responses to strain have been made with benefit to the study of this class of materials by considering solely the entropic contributions, neglecting energy changes.

In this restricted sense, certain materials may be defined as H-bond dominated solids. They form a class of solids the elastic properties of which, either in theoretical analysis or experimental studies, are found to be related in a first approximation to the density and characteristics of the hydrogen bond with only minor or negligible contributions from covalent, ionic, or van der Waals' bonds or from entropic changes. Examples are ice, rayon or other relatively disordered or low-stretch cellulosics, paper, low-stretch Nylon and similar H-bonded polymers, as well as, probably, many biological tissues and membranes.

Previous studies by the author on H-bond dominated solids based on a Morse function for the potential of the hydrogen bonds resulted in the following principal equations.[1]

(1) For a body containing a total of N_T randomly oriented hydrogen bonds, distributed with uniform density and taking part in resisting uniaxial small tensile strains, the effective number of bonds N which may be considered to resist the