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The Copolymerization of Benzene with Vinyl Acetate[1,2]

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The rate of polymerization of vinyl acetate in the undiluted state and in benzene solution was studied dilatometrically at 59.6° with α,α'-azobiscyclohexanecarbonitrile as the initiator. The rate of polymerization of undiluted monomer was in satisfactory agreement with the rates observed by other workers. In order to correlate the rate of polymerization in benzene solution with the molecular weight of the polymer, it was necessary to depart from the conventional kinetic scheme and to assume that a vinyl acetate radical can add to the benzene nucleus and the chain can then be continued by further addition of vinyl acetate monomer, leaving a benzene residue copolymerized into the vinyl acetate chain. In order to verify whether benzene copolymerizes in this fashion, vinyl acetate was polymerized in the presence of ring labeled benzene-C^{14}, and the radioactivity of the polymer obtained was in satisfactory agreement with the amount calculated from the kinetic analysis.

Introduction

This paper describes in detail the results reported in our earlier communication[5] regarding the copolymerization of benzene with vinyl acetate.

The free-radical polymerization of vinyl acetate in benzene has been studied by many workers.[6-12] The results are characterized by three features which cannot all be *simultaneously* accommodated by the conventional kinetic scheme[12,13] involving degradative chain transfer to solvent:

(i) The rate of polymerization is markedly reduced below that found in many aliphatic solvents, such as dioxane and methylcyclohexane, but similar to those found in so-called "degradative" solvents, including aromatic or allylic compounds.[14]

(ii) The order with respect to initiator remains close to one-half over a wide range of initiator concentration.

(iii) The reduction in molecular weight of the polymer is slight as compared to that in many other solvents.

As will be shown below, the magnitude of the transfer constant to benzene required to explain the observed polymerization *rates* (*i.e.*, the first two features enumerated above) is about twenty times larger than the value derived from the observed molecular weights by the conventional chain transfer scheme. The hypothesis of copolymerization is required to reconcile these observations.

Kinetic Scheme.—We employ the conventional kinetic scheme[12,13]

initiation	$I \longrightarrow 2M\cdot$	(1)
propagation	$M + M\cdot \longrightarrow M\cdot$	(2)
termination	$2M\cdot \longrightarrow P$	(3)
transfer to solvent	$M\cdot + S \longrightarrow S\cdot + P$	(4)
reinitiation	$S\cdot + M \longrightarrow M\cdot$	(5)
solvent termination	$S\cdot + M\cdot \longrightarrow P$	(6)
solvent dimerization	$2S\cdot \longrightarrow P$	(7)
transfer to monomer	$M\cdot + M \longrightarrow P + M\cdot$	(8)

where M is monomer; I, the initiator; M·, growing polymer chains; S, solvent; S·, radical formed from a solvent molecule; P, inert product. The efficiency of initiation as seen by Table I is unity. If, as suggested by Arnett[15] and others, the efficiency of initiation is less than unity, a correction factor may be included in the kinetic derivation. The constant k_3 is defined by a term $2\,k_3[M\cdot]^2$ in the rate equation for variation of $[M\cdot]$ with time and is the same as that used by Matheson, Auer, Bevilacqua and Hart[16] and by Kwart, Broadbent and Bartlett.[17]

Except in the most dilute solutions, we may neglect solvent dimerization ($k_7 \simeq 0$) and the usual steady state condition then gives the expression

$$\frac{k_1 I}{k_3[M\cdot]^2} = 1 + \frac{k_4 k_6 S}{k_3(k_5 M + k_6[M\cdot])} \qquad (9)$$

in which the concentrations of non-radical species are represented by unbracketed symbols. With the neglect of small quantities

$$-d \ln M/dt \equiv Q = k_2[M\cdot] \qquad (10)$$

Using a subscript (0) or (s) to denote absence or presence of solvent, at the same concentration of initiator, we may then rewrite equation 9 in a form identical with Kice's[13] equation 22a

$$\frac{Q_0^2}{Q_s^2} = 1 + \frac{S/M}{\alpha + \beta\, Q_s/M} \qquad (11)$$

with $\alpha = k_3k_5/k_4k_6$, $\beta = k_3/k_2k_4$, $Q_0 = k_2(k_1I/k_3)^{1/2}$.

The Initiator and Rate of Initiation.—The initiator used in this work was α,α'-azobiscyclohexanecarbonitrile, hereafter referred to as ABC. It was chosen for its relatively low rate of decomposition as compared to other azobisnitriles. The rate of initiation of vinyl acetate polymerization by ABC at 59.6° was measured by the inhibitor method

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[2] Supported by a grant-in-aid from the American Chicle Company.

[3] The Chemstrand Corporation, Decatur, Alabama.

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[5] W. H. Stockmayer and L. H. Peebles, Jr., THIS JOURNAL, **75**, 2278 (1953).

[6] A. C. Cuthbertson, G. Gee and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A170**, 300 (1939).

[7] S. Kamenskaja and S. Medvedev, *Acta Physicochemica U.R.S.S.*, **13**, 565 (1940).

[8] G. M. Burnett and H. W. Melville, *Discussions Faraday Soc.*, **2**, 322 (1947).

[9] A. Conix and G. Smets, *J. Polymer Sci.*, **10**, 525 (1953).

[10] G. M. Burnett and L. D. Loan, *Trans. Faraday Soc.*, **51**, 214, 219, 226 (1955).

[11] A. D. Jenkins, *J. Polymer Sci.*, **29**, 245 (1958), and discussion following.

[12] A. D. Jenkins, *Trans. Faraday Soc.*, **54**, 1895 (1958).

[13] J. L. Kice, THIS JOURNAL, **76**, 6274 (1954).

[14] J. T. Clarke, unpublished results in this Laboratory.

[15] L. M. Arnett, THIS JOURNAL, **74**, 2027 (1952).

[16] M. S. Matheson, E. K. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, **71**, 2610 (1949).

[17] H. Kwart, H. S. Broadbent and P. D. Bartlett, *ibid.*, **72**, 1060 (1950).

of Bartlett and Kwart.[18] Duplicate runs, with duroquinone concentrations of about 4 × $10^{-4}M$ and ABC concentrations of about 4.8 × $10^{-2}M$, gave a value for k_1 of (2.06 ± 0.10) × 10^{-5} min.$^{-1}$.

We also measured the rate of nitrogen evolution from ABC in ethyl acetate at 59.6°, obtaining $k_1 = 2.13 \times 10^{-5}$ min.$^{-1}$, in excellent agreement with the results of the inhibitor method in vinyl acetate. A similar measurement in *n*-propyl acetate at 98.5° gave $k_1 = 4.75 \times 10^{-3}$ min. If the effect of solvent is neglected, the activation energy for ABC decomposition is 34 kcal. mole^{-1}; and the interpolated rates of decomposition at 77 and 80° are in satisfactory accord with published results.[19]

Rate of Polymerization of Undiluted Vinyl Acetate.—Experimental values of Q_0 at 59.6° are given in Table I, for several initiator concentrations. These are well correlated by

$$Q_0 = 1.77 \times 10^{-2}\, I^{1/2} \qquad (12)$$

as shown in the last column. With $k_1 = 2.10 \times 10^{-5}$ min.$^{-1}$, this corresponds to a value of 2.72 ± 0.2 l.$^{1/2}$ mole$^{-1/2}$ min.$^{-1/2}$ for the combination $k_2(2k_3)^{-1/2}$, while the expression of Matheson and co-workers[16] leads to 2.36. If we combine our figure at 59.6° with that of Kwart, Broadbent and Bartlett[17] at 25°, we derive an activation energy ($E_2 - {}^1/_2\, E_3$) of 5.6 kcal. mole^{-1} as compared to Matheson's 4.7 kcal. mole^{-1}.

TABLE I

RATE OF POLYMERIZATION OF UNDILUTED VINYL ACETATE AT 59.6°

ABC × 10^2 (mole l.$^-$)	$Q_0 \times 10^3$ (min.$^{-1}$) Obsd.[a]	Calcd.
0.196	0.727	0.781
1.50	2.26	2.16
1.58	2.36	2.22
2.88	2.85	2.99
8.70[b]	5.0 ± 0.6	5.2

[a] These values are corrected for temperature differences as described in the Experimental section. [b] This run was so fast that the correction to 59.6° was much more uncertain than in the other experiments.

Rates of Polymerization of Vinyl Acetate in Benzene.—The values of Q_s are given in Table II, together with the concentrations of initiator, monomer and solvent. The values of Q_s in the fifth column are those calculated from equation 11 with $\alpha = 0.033$ and $\beta = 34.6$. These constants were obtained from the plot of Fig. 1, which corresponds to equation 11. Together with the figure quoted earlier for $k_2/(2k_3)^{1/2}$, the value of β thus found leads to a kinetic transfer constant of vinyl acetate to benzene equal to $C = k_4/k_2 = 2.0 \times 10^{-3}$. The plot of Fig. 1 is quite sensitive; if the point nearest the origin were neglected, the value of C would be changed to 2.7×10^{-3} without appreciable change in the over-all fit of the rate data. The agreement between observed and calculated rates can be seen from the fourth and fifth columns of Table II.

From the value of α we find that the ratio k_5/k_6 is about 10^{-4}, which seems reasonable.

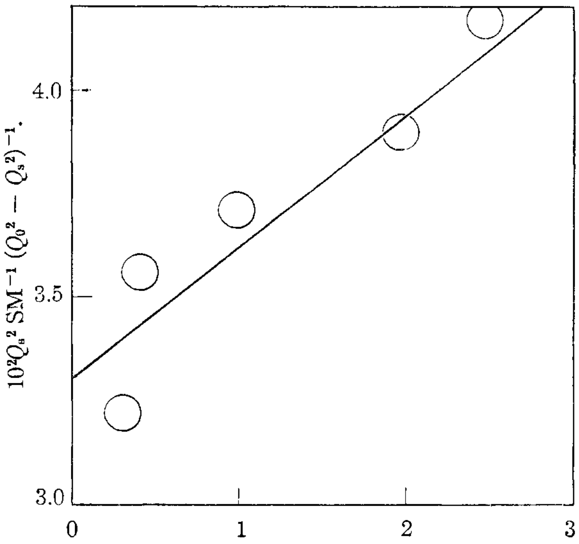


Fig. 1.—Rate of polymerization of vinyl acetate in benzene, plotted according to equation 11.

In order to compare the rate of polymerization with that calculated from equation 11 for large benzene-to-monomer ratios where dilatometric measurements are insensitive, eight ampoules of high benzene-to-monomer ratio were made up, polymerized and the polymer isolated, dried and weighed. From the time of reaction and the yield of polymer, Q_s was calculated and is also given in Table II.

TABLE II

RATES OF POLYMERIZATION OF VINYL ACETATE IN BENZENE AND RECIPROCAL DEGREES OF POLYMERIZATION

ABC × 10^2	Monomer (moles l.$^{-1}$)	Benzene	$Q_s \times 10^8$ obsd.	$Q_s \times 10^8$ calcd.	$1/\bar{P}_n \times 10^4$	$10^4 (\psi + C_m)$[a]
Dilatometric						
1.67	8.18	2.12	0.807	0.798	3.80	2.93
9.64	8.05	2.22	2.00	1.99	3.88	3.66
0.245	8.24	2.06	0.309	0.302	2.50	2.63
8.54	6.49	3.89	1.28	1.29	4.46	2.56
0.239	6.26	4.14	0.185	0.190	3.63	2.84
Gravimetric						
1.00	1.770	9.28	0.173	0.146	8.13	9.26
1.02	0.874	9.82	.114	.102	15.9	23.9
0.90	1.575	9.25	.145	.130	10.0	10.5
0.98	1.315	9.32	.180	.125	10.5	11.3
1.00	0.906	9.76	.139	.103	14.5	19.1
0.94	.848	9.82	.148	.097	15.5	18.2
1.00	.906	9.74	.135	.103	14.5	19.5
1.00[b]	.898	9.77	.138	.103	...	10.3

[a] $\psi + C_m$ defined by equation 22. [b] Contained 6 × 10^{-6} mc./mg. of ring-labelled benzene-C^{14}.

For the ampoule runs of Table II, the observed rates are faster than the rates calculated from equation 11. This is to be expected, since the assumption was made that a growing chain with an active solvent radical end does not react with a similar solvent radical but only with a growing polymer chain, *i.e.*, the mutual solvent termination constant k_7 is zero. In the ampoule experiments of Table II, the ratio of benzene to monomer is so large that

[18] P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1031 (1950).

[19] (a) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949); (b) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2663 (1949); (c) L. M. Arnett, *ibid.*, **74**, 2027 (1952).

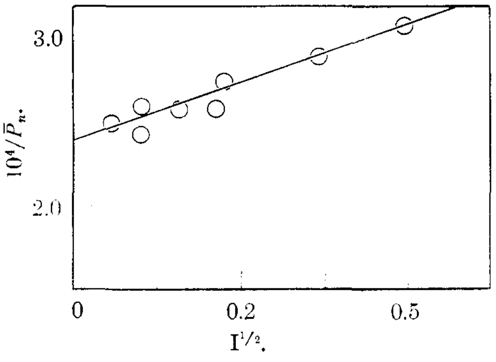


Fig. 2.—Chain transfer to monomer, see eq. 14 with S/M = 0.

this approximation is no longer completely justified. Inclusion of a non-zero value of k_7 would not appreciably alter the rate constants deduced from the dilatometric experiments by means of (11).

Degrees of Polymerization.—The reciprocal degree of polymerization is given by the conventional analysis as

$$\frac{1}{\bar{P}_n} = \frac{gk_3[\mathrm{M}\cdot]}{k_2\mathrm{M}} + C_m + C\,(\mathrm{S/M}) \qquad (13)$$

where $\bar{P}_n$ is the number average degree of polymerization, C_m the transfer constant to monomer, C the transfer constant to solvent and g a factor whose value is $2 \geqslant g \geqslant 1$, depending upon the mode of termination, *i.e.*, whether by combination of radicals ($g = 1$) or by disproportionation ($g = 2$).

Substitution of $(k_1\mathrm{I}/k_3)^{1/2}$ for [M·] in (15) yields

$$\frac{1}{\bar{P}_n} = \frac{g(k_1k_3I)^{1/2}}{k_2\mathrm{M}} + C_m + C\frac{\mathrm{S}}{\mathrm{M}} \qquad (14)$$

A plot of $1/\bar{P}_n$ against $\mathrm{I}^{1/2}$ for solvent-free runs is shown in Fig. 2. The intercept at zero initiator concentration when no solvent is present results in the transfer constant to monomer, $C_m = (2.4 \pm 0.2) \times 10^{-4}$. Clarke[14] obtained 2.5×10^{-4} for C_m at 60° with benzoyl peroxide as the initiator.

The slope of Fig. 2 corresponds to the value $g = 1.5$ in the first term in the right-hand member of equation 14, and this figure will be used subsequently. Transfer to initiator, which would produce upward curvature in Fig. 2, has been neglected.

Equation 13 may be rewritten in the form

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_n^{\,0}} + C\frac{\mathrm{S}}{\mathrm{M}}$$
$$\frac{1}{\bar{P}_n^{\,0}} = C_m + \frac{gk_3Q_s}{k_2{}^2\mathrm{M}} \qquad (15)$$

The conventional plot corresponding to the first of these equations is shown in Fig. 3, the data being found in Table II. Fortunately, the value of last term in the second of equations 15 is only about 10^{-5}, so that the value taken for g is unimportant.

The slope of Fig. 3 gives $C = 1.2 \times 10^{-4}$, or much smaller than that earlier derived from the rates. This figure may be compared with 2.4×10^{-4} measured by Chadha and Misra[20] and 2.96×10^{-4} by Palit and Das.[21] Presumably the lowest value is the most trustworthy.

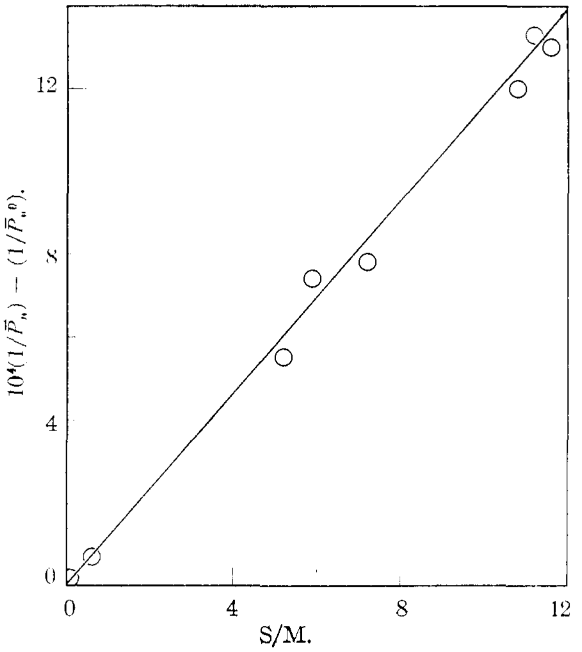
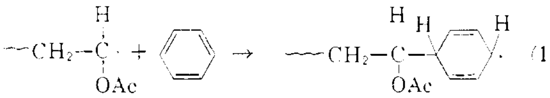


Fig. 3.—Chain transfer to benzene, see eq. 15.

Addition of Benzene to the Vinyl Acetate Chain.—The chain transfer constant computed from the molecular weights with equation 15 may now be called the "apparent" transfer constant C' and that determined from the constants α and β from the equation 11 may be called the "kinetic" transfer constant C. The latter is greater than the former by a factor of about eighteen. To reconcile this discrepancy, we postulate addition of the growing chain to the benzene ring to form a radical which can be resonance stabilized


(16)

Addition to the benzene ring was earlier proposed by Mayo[22] for certain radicals and later by Ham and Ringwald[23] to explain the gelation of vinyl acetate-vinyl benzoate bulk mixtures at roughly 50% conversion. Equation 16 in itself still is not sufficient to explain the molecular weight of the polymer. However, the addition product may now react in five ways: (a) addition to monomer; (b) addition to another benzene; (c) termination with another radical by recombination; (d) termination by disproportionation; or (e) transfer. Of these possibilities steps (b) and (c) are considered negligible.

The factor $\beta Q_s/\alpha\mathrm{M}$ lies between 0.030 and 0.26 under the conditions of our experiments. This figure gives the ratio of the rate of solvent termination to that of solvent reinitiation, or the sum of steps (c) and (d) divided by step (a). Step (a) is therefore of primary importance. It may be represented as

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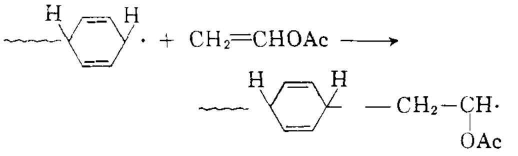
[20] R. N. Chadha and G. S. Misra, *Trans. Faraday Soc.*, **54**, 1227 (1958).

[21] S. R. Palit and S. K. Das, *Proc. Roy. Soc.* (*London*), **A226**, 82 (1954).

[22] F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).

[23] G. E. Ham and E. L. Ringwald, *J. Polymer Sci.*, **8**, 91 (1952).



(17)

Ortho addition may also occur. It has been suggested[24] that re-aromatization may take place instantaneously with simultaneous splitting out of a molecule of acetic acid, but this mechanism seems to require some severe rearrangement by hydrogen atoms. This possibility could be investigated with tritium-labeled benzene. In any case, it seems likely that during precipitation and drying of the polymer most of the cyclohexadiene rings would be oxidized to aromatic form.

Analysis of the Polymer.—From the familiar relation

$$d S/dM = C S/M \qquad (18)$$

it may easily be seen that with $C \simeq 2 \times 10^{-3}$, the initial polymer made from a 10% solution of vinyl acetate in benzene should contain about 2% of combined benzene or cyclohexadiene residues, which seems a detectable amount. We nevertheless failed to identify such residues in our polymer samples by combustion analysis, determination of unsaturation with iodine monochloride or by infrared absorption. However, radioactivity was found in the polymer when ring-labeled benzene $-C^{14}$ was used in the polymerizing solution.

A solution of vinyl acetate in C^{14}-labeled benzene was polymerized (see Table II) and the resulting polymer was carefully washed to remove residual radio-benzene. The specific activity did not decrease through four successive purifications of the polymer and corresponded to a ratio $(S/M)_p$ in the polymer of 0.030. If the benzene had been present only at chain ends, the value of $(S/M)_p$ would have been 0.0014, which differs from that obtained by a factor of about 20. From equation 18 the value of C is calculated to be 2.8×10^{-3}, in good agreement with the value obtained earlier from the rates of polymerization. This corresponds to a copolymer reactivity ratio r_1 of about 350 with vinyl acetate as monomer 1; the other reactivity ratio r_2 must of course be very small.

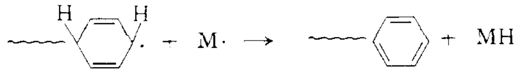
Discussion

Copolymerization having been demonstrated, it is now necessary to reconsider the degree of polymerization. Two distinct reactions between vinyl acetate radical and benzene can now be explicitly recognized:

$$M\cdot + S \longrightarrow S\cdot \quad \text{copolymerization, rate constant } Ck_2 \qquad (19)$$

$$M\cdot + S \longrightarrow X\cdot + P \quad \text{Conventional transfer, rate constant } C'k_2 \qquad (20)$$

where X· stands for $C_6H_5\cdot$ or $C_6H_7\cdot$. Since we must have $C' << C$, the reactivity of X· in regeneration and termination is of no importance. We assume that the "cross termination" step 9 is a disproportionation with re-aromatization of the benzene residue



(21)

Steady state analysis then gives the reciprocal degree of polymerization (still with $k_7 = 0$)

$$\frac{1}{\bar{P}_n} = C_m + \psi + C' \frac{S}{M}$$

where

$$\psi = \frac{k_1 I}{M\,Q_s} \left\{1 - (g - 1)\frac{Q_s^2}{Q_0^2}\right\} \qquad (22)$$

The factor in braces is nearly unity for the experiments of Table II, whatever the value of g. In the last column of that table are found the values of $C_m + \psi$ calculated from the above expression. The difference between these values and the observed values of $1/\bar{P}_n$ should represent the term C' S/M, and from the dilatometric runs we thus find that C' is of the order of magnitude of 10^{-4}. However, the results are not precise enough to yield a reliable value of this constant.

It is seen that for each of the ampoule runs (and for one of the dilatometric runs) the value of $C_m + \psi$ actually exceeds the observed value of $1/\bar{P}_n$, on the average by about 20%. This may be partly due to a systematic error in our viscosity-molecular weight relation, but it is more probably due to our consistent neglect of reaction 7. When the previous discrepancy of a factor of 18 is recalled, the present agreement seems highly satisfactory.

It remains for us to comment briefly on the results and opinions of several other workers. Burnett and Loan[10] have measured rates of vinyl acetate polymerization in benzene at several temperatures, including 60°, with azo-bis-isobutyronitrile (AIBN) as initiator. A comparison of their results with ours can be made with the aid of the decomposition rates of AIBN, given by van Hook and Tobolsky,[25] and we find that if ABC and AIBN are assumed to have comparable efficiencies of initiation the rates of polymerization in undiluted monomer agree well. In benzene solution, however, our rates are definitely greater; for example, from our kinetic constants the rate in 90% vinyl acetate-10% benzene is calculated to be about twice that observed by Burnett and Loan. In view of the difficulties of purification in this system (see Experimental section) it seems likely that their results are influenced by traces of a retarder and therefore that their unusually high overall activation energy (some 37 kcal. mole^{-1}) refers to a partly unknown kinetic system.

Jenkins,[12] from a study of Burnett and Loan's results, concludes that conventional transfer to solvent gives an adequate account of the kinetics. This statement, as remarked in our introduction, is valid for the polymerization *rates* over a limited range of initiator concentrations, but it cannot be supported if the molecular weights of the polymer are also considered. With reference to the latter, Jenkins has suggested that copolymerization of benzene would alter the relation between intrinsic viscosity and molecular weight but since the benzene/vinyl acetate ratio in the polymers was always

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[24] W. M. D. Bryant, private communication.

[25] J. P. van Hook and A. V. Tobolsky, THIS JOURNAL, **80**, 779 (1958).

less than 0.03, this influence would be entirely negligible, as can be seen from results[26] for other copolymers.

Since completion of this work, Szwarc and his collaborators[27–29] have measured "methyl affinities" (relative rates of addition of methyl radicals) for a large number of aromatic hydrocarbons and ethylene derivatives. They find that the methyl affinity of vinyl acetate is about 100 times that of benzene at 65°. This may be compared to our figure of $1/C \cong 400$ for the relative rates of reactions 2 and 22 at 60°. It is interesting to note that the methyl affinities of styrene and vinyl acetate[28] are about in the ratio 25, while the relative reactivity of these monomers toward vinyl acetate radical is[30] about 100. Thus the effect of radical structure on the relative rates gives a factor of about four in each case.

Experimental

Polymerization Apparatus.—The rates of polymerization at low benzene-to-monomer ratio were determined in a twin-capillary dilatometer made of Pyrex glass. The capillaries are Precision Bore Capillary Tubing obtained from the Phoenix Precision Instrument Company, Philadephia, Pennsylvania, with a given and measured diameter of 0.0660 ± 0.0002 inches. Loading of the dilatometer was performed under vacuum, the ampoules of purified benzene and partly purified vinyl acetate (see below) being opened by magnetic hammers within the vacuum system. Monomer was pre-polymerized by illumination with ultraviolet light in a bulb to which benzoyl peroxide had been added, and after about 25% conversion the remaining monomer was distilled into another bulb containing a weighed quantity of ABC initiator. After the desired quantity of benzene was distilled into the same bulb and the contents were thoroughly mixed, these were decanted to the dilatometer, which was then sealed off and transferred to the temperature bath. The height of liquid in the dilatometer capillaries was periodically read with a cathetometer to 0.01 cm. and the time of reading was noted to within 0.5 sec.

The solutions for the gravimetric runs of Table II were made up and loaded into ampoules in a similar way.

Rates of Initiator Decomposition.—A gas buret apparatus consisting of a reaction bulb, water condenser, gas buret, levelling bulb, and a small-open-end manometer was used to measure the amount of nitrogen evolved during the decomposition of ABC.

Dilatometer Calculations.—The data of Starkweather and Taylor,[31] Powers[32] and the interpolation of Matheson and co-workers were used to calculate the densities of vinyl acetate monomer and polymer. The benzene values were calculated from the density formula given in the International Critical Tables.[33]

If the change in volume on mixing benzene, vinyl acetate and polyvinyl acetate may be neglected, then the rate of change in volume of the dilatometer contents with time is directly proportional to the original amount of monomer in the dilatometer and to the rate factor Q.

Since the polymerization is exothermic, the temperature within the polymerizing medium is higher than that of the thermostat. Consider the dilatometer to be a sphere of radius a, with a constant source of heat inside the sphere, and the sphere immersed in a constant temperature bath. The excess temperature θ at any point r in the sphere can be obtained from the solution of the heat conduction equation as given by Carslaw and Jaeger.[34] If θ is averaged by evaluating

$$\langle\theta\rangle = \int_0^a 4\pi r^2\theta \mathrm{d}r \Big/ \int_0^a 4\pi r^2 \mathrm{d}r$$

it is found that after about 250 seconds the dilatometer essentially reaches a thermal steady state given by

$$\langle\theta\rangle = \frac{(-\Delta H)QV_0'a^2}{15V_0W\bar{C}_\mathrm{p}\,\kappa} = \frac{237QV_0'}{V_0} \quad (Q \text{ in min.}^{-1})$$

where V'_0 is the volume of vinyl acetate in the dilatometer, V_0 the total volume in the dilatometer, W the molecular weight of vinyl acetate, C_p specific heat capacity at constant pressure and ΔH the enthalpy of polymerization per mole.

The ratio a^2/κ, involving the equivalent sphere radius of the dilatometer and the thermal diffusivity, was determined by comparing the observed transient temperature–time curves of the dilatometer with the theoretical curves given in Carslaw and Jaeger.

The energy of activation for Q is

$$E_\mathrm{a} = RT^2\,\mathrm{d}\ln Q/\mathrm{d}T$$
$$= E_2 - \frac{1}{2}E_3 + \frac{1}{2}E_1 \cong 22.5 \text{ kcal. mole}^{-1}$$

from results in the text. The temperature correction is then approximately

$$Q \cong Q(\text{obsd.}) \exp(-E_\mathrm{a}\langle\theta\rangle/RT^2)$$
$$\cong Q(\text{obsd.}) \exp(-24\,QV_0'/V_0)$$

Purification of Materials. Benzene.—Mallinckrodt reagent benzene was shaken successively for about an hour each with concentrated sulfuric acid, distilled water twice, 6 N sodium hydroxide, distilled water twice again. The wet benzene was then distilled through a three-foot glass column to remove a major part of the water. Absolute ethyl alcohol was then added to approximately the concentration of the benzene–alcohol azeotrope, and the solution was redistilled. By the low boiling distillation, any non-azeotrope forming impurities should have been left behind. The middle fraction was again shaken with distilled water to remove the alcohol and again redistilled to remove excess water and traces of alcohol. The benzene was then distilled through a six-foot Kraus type still over sodium metal. Fractions were removed when the benzene vapor remained at a constant temperature (corrected for barometric pressure) in the still head for over an hour. Four top and three bottom fractions were removed until the top and bottom fractions recorded the same temperature. This temperature was not recorded. The benzene was then redistilled from lithium aluminum hydride under an atmosphere of nitrogen in order to remove any traces of water and any peroxides that may have formed. The final distillation was made under vacuum directly into the ampoules.

Preparation of α,α' Azobiscyclohexanecarbonitrile.—The procedure of Thiele and Heuser[35] and of Dox[36] was used to prepare this compound. The method of preparation has been described in reference 19.

Vinyl Acetate.—Commercial vinyl acetate was obtained from the Niacet Chemical Division, United States Vanadium Corporation, Niagara Falls, New York, containing hydroquinone as the stabilizer. Two methods of purification were used. The first method was found to be inadequate, in that trace amounts of a retarder were present and could not be entirely removed by more prepolymerization. In the second method it was removed by fractional distillation.

Method I.—The crude vinyl acetate was first distilled through a four-foot glass helix packed column of approximately 30 theoretical plates, the middle fraction was then polymerized in bulk by refluxing the monomer while being irradiated by ultraviolet light to roughly 10% conversion. The monomer was crudely fractionated from the residue, then distilled through the three-foot still under an atmosphere of nitrogen, into the ampoules.

Method II.—The crude monomer was distilled through a 160 theoretical plate Podbielniak column with the take-

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off set at ten seconds every hour under an atmosphere of "pre-purified" nitrogen. The monomer was collected in ampoules described elsewhere and sealed off under reduced pressure.

In contrast to our experience, the vinyl acetate obtained by Matheson and co-workers[16] from Eastman Kodak Company contained an inhibitor which could be removed by distillation from a prepolymerized mixture. The identity of these retarding and inhibiting impurities is open to speculation.

The rates of polymerization after the two methods of purification of vinyl acetate at 25° with 0.105 molar benzoyl peroxide as initiator are compared below

Method	Rate of polymeriz. $\times 10^5$ (mole l.$^{-1}$ sec.$^{-1}$)
I	4.21
II	7.94
Matheson's Table II	
Second cut pre-irradiated	8.1
Best sample	8.5
Swain and Bartlett[37]	8.4

Duroquinone.—The duroquinone, a gift from Professor P. D. Bartlett, had been prepared by Dr. Harold Kwart according to the method of "Organic Synthesis"[38] and was used without further purification.

Precipitation of Polymer.—The concentration of polymer in solvent was adjusted with acetone so that when added dropwise to well stirred, filtered *n*-hexane with a 60–70° boiling range, a fibrous precipitate was formed. The polymers from the very dilute ampoule determinations were first concentrated by blowing air over the solution. The polymer thus obtained was first allowed to stand for several hours at room temperature in a vacuum desiccator charged with anhydrous phosphorus pentoxide, then dried to constant weight in a 60° oven. The ampoule determinations were further dried in a vacuum oven at 60°.

Molecular Weight Determination.—Solution viscosities in acetone at 25° were determined in an Ostwald–Fenske viscometer and kinetic energy corrections were applied. The inherent viscosities, $[\eta] = c^{-1}\ln(\eta/\eta_0)$, were converted to intrinsic viscosities by the equation (c in grams per deciliter)

$$[\eta] = \{\eta\} + 0.14\,\{\eta\}^2 c$$

and then to number-average degrees of polymerization by the relationship

$$\log \bar{P}_n = 3.24 + 1.40 \log [\eta] \qquad (23)$$

The latter equation was obtained in this Laboratory by Howard[39] as follows. From light scattering measurements on a series of low-conversion polyvinyl acetates, both fractionated and unfractionated, and with proper allowance for the minor effects of polydispersity, he obtained the equation

$$\log \overline{\mathrm{M}}_v = 5.44 + 1.40 \log [\eta] \qquad (24)$$

for polymers with M less than 4×10^5. Since low-conversion polyvinyl acetate has a molecular weight essentially controlled by transfer reactions, the "most probable" molecular weight distribution will be obtained in unfractionated samples, and with the viscosity exponent $a = 1/1.40 = 0.71$, this yields[40]

$$\overline{\mathrm{M}}_v/\overline{\mathrm{M}}_n = 1.85$$

which with (24) leads to (23). It should be remarked that equation 24 gives results somewhat different from the relation of Wagner,[41] which was based on osmotic molecular weights of fractionated high-conversion commercial polymer.

Radioactivity Determination.—The ampoule of polymer containing radiobenzene was opened, the polymer was precipitated and dried as described above. A portion of the polymer was set aside and labeled A. The residue was dissolved in 40 ml. of acetone, evaporated down to less than one ml., reprecipitated, dried and a portion set aside and labeled B. This procedure was repeated twice more, then the portion D was dissolved in 40 ml. of reagent benzene and evaporated to near dryness five times, then precipitated into *n*-hexane and dried to constant weight in a vacuum oven. The activities of CO_2 obtained from each of the samples A to D were determined in duplicate by Mrs. Clare M. Regan. The analyses of sample B were vitiated by a leak in the gas system, but those of samples A, B, D gave respectively 13.3, 13.2 and 15.1×10^{-3} μcurie/millimole. The average of these figures corresponds to the figure of 0.030 for $(S/M)_p$ quoted in the text.

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Hypochromism in Polynucleotides[1]

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The change in light absorption which occurs when a polymer changes from an ordered (native) to a disordered (denatured) structure is attributed to the interaction between the dipoles induced in the chromophores by the light. Calculated values for the relative absorption coefficients of native deoxyribonucleic acid (DNA) and its mononucleotides are consistent with the experimental fact that the light absorption of native DNA is about 60% of the absorption of its mononucleotides.

Introduction

The ultraviolet light absorption of a polynucleotide is considerably less than the sum of the absorptions of its constituent nucleotides. Furthermore, the absorption of the polymer is very sensitive to the environment. High temperature, high concentration of urea, temporary extremes of pH and low ionic strength all cause an increase in the molar absorption coefficient. However, the shape of the absorption curve and the wave length maximum are not affected. Hydrolysis of the polymer causes similar changes. These results have been presented in detail previously.[2–5] Recent experiments have used this change in light absorption to study the

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