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Copolymerization of Vinyl Chloride and Sulfur Dioxide. II. Copolymerization Rates and Copolymer Compositions

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ABSTRACT

The rate of copolymerization of vinyl chloride (VC) with sulfur dioxide and the composition of the poly(vinyl chloride sulfone) formed have been measured for comonomer liquid mixtures with $x_{VC} = 0.1$ to 1.0 and over the temperature range -95 to +46°C. Polymerization was initiated by γ-irradiation (-95 to +46°C) and with the t-butyl hydroperoxide/SO_2/methanol redox system (-95 to -18°C). The copolymerization rates and copolymer compositions indicated two distinct temperature regions, with a change in mechanism around 0°C. For radiation initiation below 0°C, the rate versus comonomer composition relationship showed a maximum at an x_{VC} value which increased with increasing temperature. Above 0°C, the rate decreased with increasing temperature and was greatly retarded by SO_2. No high molecular weight copolymer or VC homopolymer was formed on irradiation of comonomer mixtures above ~ 55°C.

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INTRODUCTION

Vinyl chloride is one of the few monomers (M) which copolymerize with sulfur dioxide (S) by a free radical mechanism to form variable-composition polysulfones with the empirical formula $M_{\overline{n}}S$, where $\overline{n} > 1.0$. In contrast, olefins [1] give polysulfones with $\overline{n} = 1.0$, independent of (a) comonomer composition in the liquid phase and (b) polymerization temperature. The copolymerization of each olefin with sulfur dioxide is characterized by a ceiling temperature T_c, above which high molecular weight polymer is not formed [2]. Monomers with strong electron-withdrawing substituents, such as methyl methacrylate [3] and acrylonitrile [4], only undergo homopolymerization in liquid sulfur dioxide.

Marvel and Glavis [5] reported the first preparation of poly(vinyl chloride sulfone) and also of poly(vinyl bromide sulfone); in both cases the copolymer contained, on average, two vinyl halide units for each sulfur dioxide unit. "Aged" paraldehyde or the active component, peracetic acid, in large amounts, was used as the catalyst and the reaction carried out between 0° C and room temperature. The structure was assigned predominantly to $-SO_2CHClCH_2CHClCH_2SO_2-$ by Marvel and Dunlap [6] on the basis of the hydrolysis products in 20% aqueous sodium hydroxide. Ascaridole with HCl or HBr was also found to be an effective catalyst (apparently at room temperature) by Kharasch and Sternfeld [7].

Schneider, Denaxas, and Hummel [8] made the first examination of the effect of copolymerization temperature and comonomer composition upon the composition of poly(vinyl chloride sulfone). They used γ-radiation to initiate the copolymerization and found that the composition of the copolymer was $\overline{n} \approx 1.5$ at -75°C and $\overline{n} \approx 2$ at +20°C, independent of comonomer composition from $x_{VC} = 0.10$ to 0.84.

Suzuki, Ito, and Kuri [9] also studied the effect of temperature and comonomer composition on the copolymerization rate and copolymer composition for vinyl chloride and sulfur dioxide, using γ-radiation for initiation. Only a slight dependence of copolymer composition on comonomer feed was found, even at room temperature. The copolymer composition decreased from $\overline{n} = 3.6$ to $\overline{n} = 1$ as the polymerization temperature was decreased from +20 to -78°C. They also claimed that copolymerization proceeded in the solid state. The information available on poly(vinyl chloride sulfone) up to 1970 has been reviewed by Ito, Ito, and Muyashige [10].

We have made a detailed investigation of the copolymerization of vinyl chloride and sulfur dioxide in the liquid phase from -95 to +46° C. The formation of two comonomer complexes, $VC\text{-}SO_2$ and $VC\text{-}(SO_2)_2$, was demonstrated [11]. The importance of depropagation reactions was indicated in a preliminary publication [12]. In this paper we report measurements of the rate of copolymerization and of the copolymer composition as functions of comonomer composition from

x_{VC} = 0.1 to 1.0 for bulk and diluted comonomer mixtures. γ-Irradiation was used to initiate the copolymerization at, and above, 0°C and the t-butyl hydroperoxide/methanol/SO_2 redox system [13] below 0°C in order to minimize radiation-induced dehydrochlorination.

Recently Matsuda and Thoi [14] reported the copolymerization of vinyl chloride and sulfur dioxide in the temperature range 0-50°C using azobisisobutyronitrile and cumene hydroperoxide as initiators. Their results complement the earlier work of Schneider et al. [8] and Suzuki et al. [9] and can be compared with the comprehensive study reported in this paper.

These results will be used in combination with comonomer sequence distributions, determined from ^{1}H NMR spectra [15], to examine the applicability of various copolymerization models throughout the range of polymerization temperatures in the following paper.

EXPERIMENTAL

Preparation of Comonomer Mixtures

Vinyl chloride (polymerization grade, free of inhibitor, kindly supplied by I.C.I. Australia) was dried over 3A molecular sieves and dissolved "permanent" gases removed by repeated freeze-pump-thaw cycles. Gas chromatographic analysis did not detect any impurities above 10 ppm. Sulfur dioxide (Matheson Co.) was dried over molecular sieves and phosphorous pentoxide. The monomers were measured as vapors (mp: SO_2 = -10°C, VC = -14°C) in a 4-dm^3 bulb at a standard temperature. The bulb was calibrated by condensing and weighing (with buoyancy corrections) measured pressures of each monomer, and to allow for nonideal gas behavior, the equation $P/n = A + bP$ was used, where P = pressure, n = number of moles of monomer, and A and B are the first and second virial coefficients, respectively. Comonomer mixtures (≈0.1 mol = 6 g) were prepared by condensing the measured quantities of each monomer vapor into a glass ampule.

Radiation Initiation

Irradiations were carried out in the pond facility of the Australian Atomic Energy Commission Research Establishment in a uniform field of cobalt-60 γ radiation at dose rates from 0.34 to 0.56 Mrd/h. The radiation dose rate varied due to (1) the decay of ^{60}Co activity with time and (2) different attenuations of various constant-temperature irradiation rigs. Therefore, all kinetic results were converted to a standard dose rate of 0.42 Mrd/h at which most work was done, using the measured dose rate exponent of 0.8. Fricke dosimetry ($G_{Fe^{3+}}$ = 15.5) was used to measure dose rates.

Chemical Initiation

t-Butylhydroperoxide (Koch-Light laboratory reagent containing 70% t-BuOOH and 30% di-t-butyl peroxide) dissolved in distilled methanol (25 mL/100 mL) was used for chemical initiation and gave a very rapid copolymerization rate at low temperature. In order to ensure that copolymerization only occurred at the required temperature, the initiator solution was freeze-thaw degassed in a section of the ampule which was separated from the comonomer mixture by a thin glass membrane. After temperature equilibration the membrane was broken and the initiator solution mixed with the monomers.

Characterization of Copolymers

Chemically initiated polymerizations were stopped by transferring the reaction mixture into a large volume of methanol. Mixtures initiated by radiation were frozen and stored at 77 K until separation to prevent postirradiation effects. The copolymers were separated by decanting and evaporating the methanol and residual monomers, followed by drying in a vacuum oven at 30°C to constant weight ($>$ 12 h). Higher temperatures could not be used due to thermal dehydrochlorination of the copolymers, especially those with $\bar{n} < 2$. Copolymerization rates were measured by the copolymer yields after various polymerization times.

Microanalyses were carried out for all component elements in representative samples. Infrared spectra were obtained from KBr disks (2 mg/200 mg) with a Perkin-Elmer 225 spectrophotometer. The model compounds dimethyl sulfone, diethyl sulfone, divinyl sulfone, p-toluene sulfonyl chloride, 1,2-bis(methyl sulfonyl) ethane, and 1,1-poly(ethylene sulfone) was used to assist in the assignment of the absorptions. 100 MHz NMR spectra were recorded at 55°C with a JEOL-JNM-MH-100 spectrometer using filtered 10% wt/vol solutions of the copolymers in perdeuterated acetone, tetrahydrofuran (THF), and dimethylsulfoxide (DMSO).

The viscosities of copolymers with $\bar{n} = 4$ and 16 were measured in THF solutions at 25°C with a Ubbelohde viscometer. The molecular weights of copolymers prepared by t-BuOOH initiation were measured by ^{1}H NMR. The ^{1}H NMR spectra showed a singlet resonance from the nine protons in a t-BuO fragment on the chain, and comparison of the area of this resonance with peaks due to vinyl chloride enabled measurements of number-average degrees of polymerization, $\overline{DP}_n$, up to ≈1000.

RESULTS

Measurement of Copolymer Composition

Poly(vinyl chloride sulfone) may be represented by the empirical formula $(CH_2CHCl)_{\bar{n}}SO_2$. The elemental compositions of copolymers prepared under a variety of conditions were determined by microanalysis and it was found that $\bar{n}$ increased from ≈2 at 0°C to > 4 at 46°C depending on the comonomer composition. Below 0°C the value of $\bar{n}$ decreased toward 1 with decreasing temperature, but increasing discrepancies between $\bar{n}$ values calculated from different pairs of elements, especially for copolymers prepared by radiation initiation, indicated a variation in chemical formula. This was shown to be due to dehydrochlorination [16]. The microanalysis results were found to fit the empirical formula $(CH_2CHCl)_x(CH{=}CH)_ySO_2$. The true $\bar{n}$ for dehydrochlorinated copolymers is $\bar{n} = x + y$, as dehydrochlorination was shown to occur subsequent to formation of the polymer and not during polymerization.

Infrared Spectra

The infrared spectra of the copolymers were also used to measure the value of $\bar{n}$ and to confirm the presence of unsaturated $-CH{=}CH-$ units. These spectra, when compared with the spectrum of pure poly(vinyl chloride), showed that increasing SO_2 content in the copolymer resulted in development of the intense absorptions characteristic of the $C-SO_2-C$ group, particularly the $O{=}S{=}O$ asymmetric stretch at 1300 cm^{-1} (1), symmetric stretch at 1135 cm^{-1} (2), bend at 550 cm^{-1} (3), and wag at 485 cm^{-1} (4) and the $C-S-C$ asymmetric stretch at 770 cm^{-1} (5) as shown in Fig. 1. The infrared spectra of copolymers with $\bar{n} > 2$ could be regarded as the superposition of the spectra of poly(vinyl chloride) and the $C-SO_2-C$ group.

The ratio of the absorbance of the CH_2 bending vibration at 1423 cm^{-1} (7) to the $O{=}S{=}O$ symmetric stretch at 1135 cm^{-1} was used to determine the copolymer composition as shown in Fig. 2. The calibration plot using $\bar{n}$ values determined by microanalysis and NMR is shown in Fig. 3 and is a good linear relationship. For copolymers with $\bar{n} < 2$ the absorptions from the $C-SO_2-C$ group were very intense and overlapped the weaker vinyl chloride absorptions, hence compositions could not be measured accurately. Also, the CH_2 bending vibration was apparently split into two peaks, with the second peak at 1395 cm^{-1} attributed to CH_2 which is in the chain position α to SO_2.

The presence of trans $-CH{=}CH-$ units in samples prepared at low temperatures by radiation initiation was shown clearly by the absorption at 1610 cm^{-1} [Peak 6 in Fig. 1(D)], the assignment being confirmed by the spectrum of divinyl sulfone. However, it was partially overlapped by a broad water peak at 1630 cm^{-1} (water absorbs strongly to the polar sulfone group and was difficult to remove completely from copolymers with $\bar{n} < 2$ without decomposing the polymer), which prevented accurate quantitative measurement of y by this method.

NMR Spectra

The ^{1}H NMR spectra of poly(vinyl chloride sulfone)s are complex and the detailed analysis using copolymers prepared from vinyl

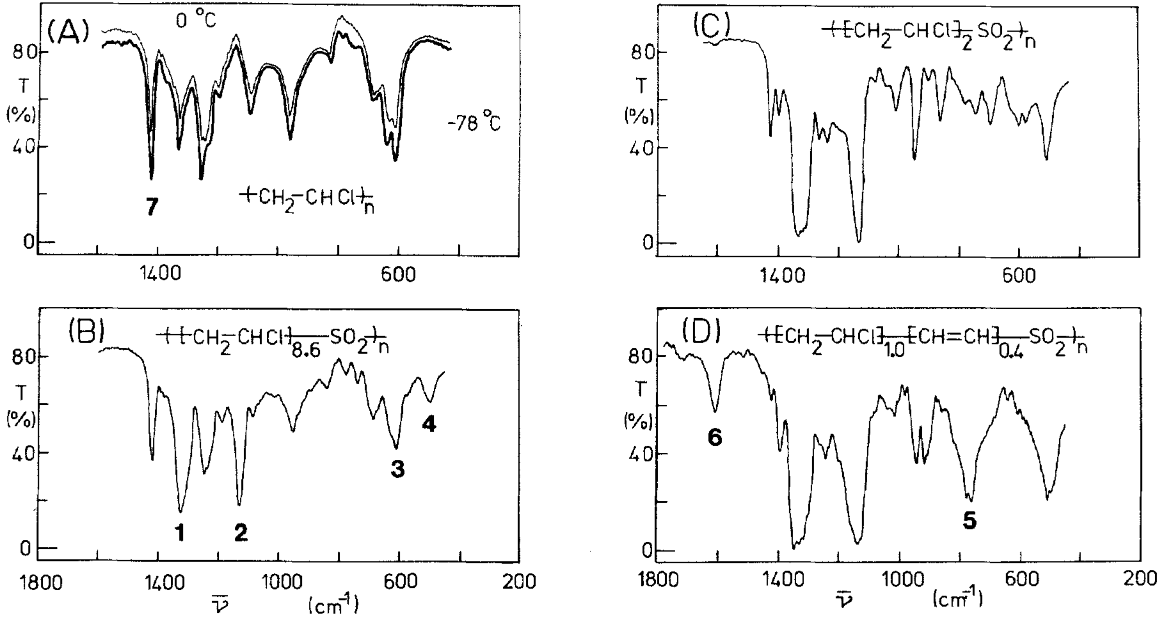


FIG. 1. Infrared spectra. A: Poly(vinyl chloride) prepared by radiation initiation in bulk at 0 and -78° C. B and C: Poly(vinyl chloride sulfone)s with $\bar{n}$ = 8.6 and 2.0, respectively. D: Poly(vinyl chloride sulfone) containing 35% dehydrochlorinated vinyl chloride units, i.e., x = 1.0, y = 0.4, $\bar{n}$ = 1.4. The poly(vinyl chloride sulfones)s were all prepared by radiation initiation (at different temperatures). T = transmittance. Explanation of peak numbers in text.

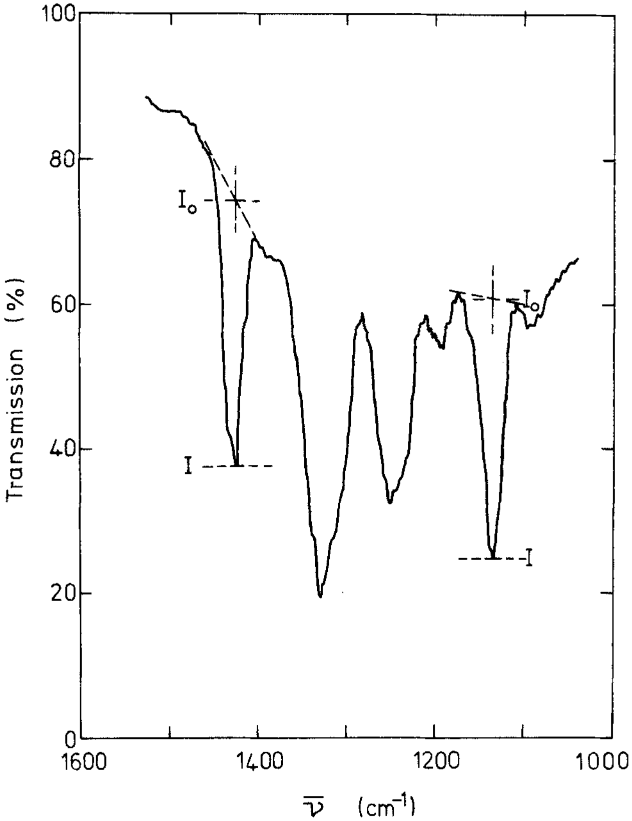


FIG. 2. Determination of composition of poly(vinyl chloride sulfone)s with $\bar{n} > 2$ from absorbances of CH_2 bending (1423 cm^{-1}) and O=S=O symmetrical stretch (1140 cm^{-1}) absorptions in infrared spectra.

chloride-β,β-d_2 is discussed elsewhere [15]. Macroscopic copolymer compositions (x, y, and $\bar{n}$ values) were obtained from the PMR spectra by comparing the areas (A) of peaks assigned to the different comonomer diad sequences. These diads give rise to five resonance regions which are multiplets due to vicinal and geminal proton coupling and monomer and configurational sequence effects. These resonances were assigned to the various methylene, methine, and olefinic protons as shown in Table 1. The five peaks can be seen in Fig. 4.

For copolymers which had not undergone dehydrochlorination ($A_5 = 0$), the composition could be determined from any of the following relationships:

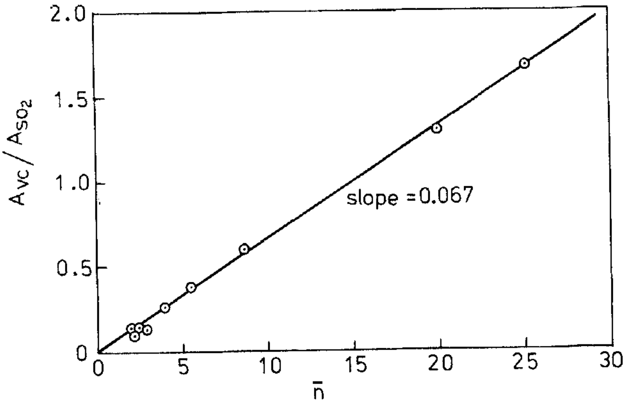


FIG. 3. Calibration plot for infrared method of determining copolymer composition. A_{VC} and A_{SO_2} are absorbances of absorptions shown in Fig. 2.

TABLE 1. Assignment of Resonance Areas in 100 MHz ^{1}H NMR Spectra of Poly(vinyl chloride sulfone) for Determination of Copolymer Composition and Molecular Weight (V = $-CHCl-CH_2-$)

No.	Chemical shift δ_{ppm}		Abbreviation	Proton type
1	2.0-3.0	$-CHCl-C\overset{*}{H}_2-CHCl-CH_2-$	VV	PVC methylene
2	3.6-4.4	$-CHCl-C\overset{*}{H}_2-SO_2-$	VS	α-Sulfonyl methylene
3	4.4-4.8	$-CHCl-CH_2-C\overset{*}{H}Cl-CH_2-$	VV	PVC methine
4	5.4-6.2	$-SO_2-C\overset{*}{H}Cl-CH_2-$	SV	α-Sulfonyl methine
5	7.8-8.2	$(-SO_2)-CH=C\overset{*}{H}-SO_2-$	ES SE	α-Sulfonyl olefinic
6	1.8	$(C\overset{*}{H}_3)_3C-O-SO_2-$	t-BuO	γ-Sulfonyl-t-butoxy
7	0		TMS	Standard

[a] Asterisks indicate the protons producing the NMR peak.

$$\bar{n} = 1 + A_1/A_2 = 1 + A_3/A_4 = 1 + A_1/2A_4 = 1 + 2A_3/A_2$$
$$\text{(i)} \qquad \text{(ii)} \qquad \text{(iii)} \qquad \text{(iv)}$$

Equation (iii) gave the most reliable results as Peaks 1 and 4 were usually well resolved. Peaks 2 and 3 partially overlapped, but their individual areas could be obtained from

$$A_1 = 2A_3 \text{ and } A_2 = 2A_4$$

A detailed examination of the dehydrochlorination showed that under normal experimental conditions only SVS triad sequences dehydrochlorinated (S = sulfur dioxide, V = vinyl chloride units in the chain). The composition of dehydrochlorinated copolymers could therefore be measured by

$$x = (A_1 + 2A_4)/(A_5 + 2A_4)$$

$$y = A_5/(A_5 + 2A_4)$$

Analysis of the ^{1}H NMR spectrum as detailed above was the best

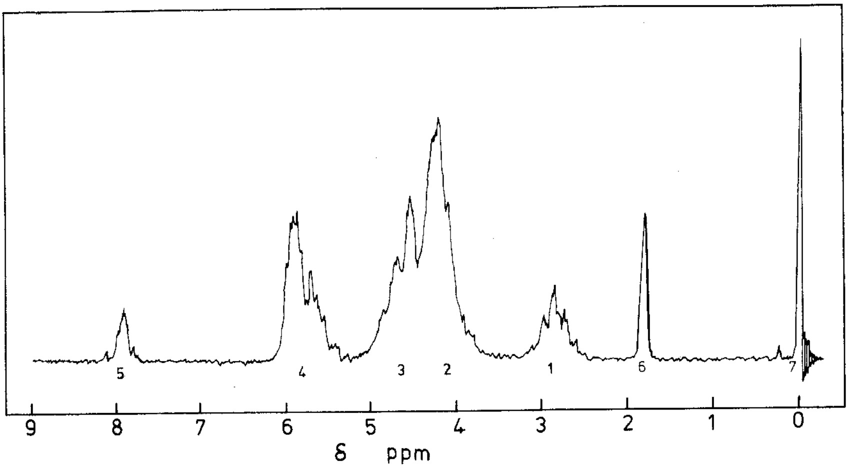


FIG. 4. 100 MHz, ^{1}H NMR spectrum of poly(vinyl chloride sulfone) prepared by initiation with t-BuOOH at -45° C, showing resonances used for analysis of the composition of the copolymer. (Assignment of resonances is given in Table 1.)

TABLE 2. Copolymerization Rates for Initiation by t-Butyl Hydroperoxide[a]

Temperature (°C)	[t-BuOOH][a] (vol%)	$(x_{VC})_m$	R_p (%/h)
-18	6.0	0.2	0.12
		0.4	0.78
		0.6	1.31
		0.8	0.65
-45	4.5	0.2	0.61
		0.4	0.57
		0.6	0.47
		0.8	0.25
-78	3.0	0.2	82.2
		0.4	15.8
		0.6	20.1
		0.8	0.7
-95	3.0	0.6	78
		0.8	42

[a] a = 20 mL t-BuOOH (70%) in 100 mL methanol.

method for determining the composition of poly(vinyl chloride sulfone) for all values of x, y, and $\bar{n}$. It was particularly useful for $\bar{n} < 2$ and $y > 0$.

Rate of Copolymerization

Chemical Initiation

t-Butyl hydroperoxide in methanol was used as initiator at low temperatures to avoid the dehydrochlorination which occurred with radiation initiation. The copolymerization rates (R_p) for different conditions are given in Table 2 and Fig. 5. The main features are: (1) the copolymerization rate increased with increasing SO_2 concentration in the comonomer mixture below -18°C; (2) for a fixed comonomer composition the rate decreased rapidly with increasing temperature; (3) the copolymerization rate was negligible above -18°C

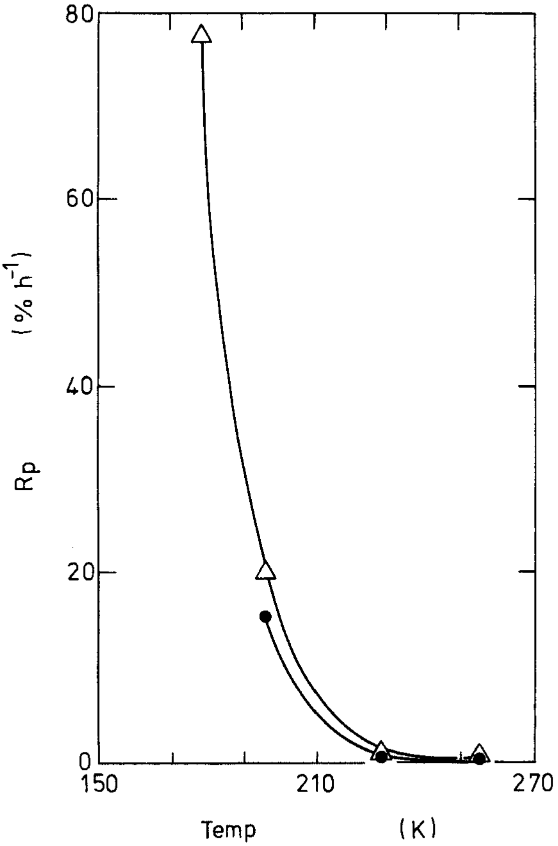


FIG. 5. Copolymerization rate (R_p) for initiation by t-BuOOH/ CH_3OH (3.0 mL/100 mL) as a function of polymerization temperature. (△) $x_{VC} = 0.60$; (●) $x_{VC} = 0.40$.

with t-BuOOH initiation, whereas the rate of the radiation-induced reaction was appreciable for VC-rich mixtures; and (4) the chemically initiated reaction was much faster than the radiation-induced reaction below -45°C.

Radiation Initiation

Figure 6 shows the conversion as a function of irradiation time for several temperatures, comonomer compositions, and radiation dose rates. These three variables all affected the copolymerization rate. The observed linear relationships (below 20% conversion) are

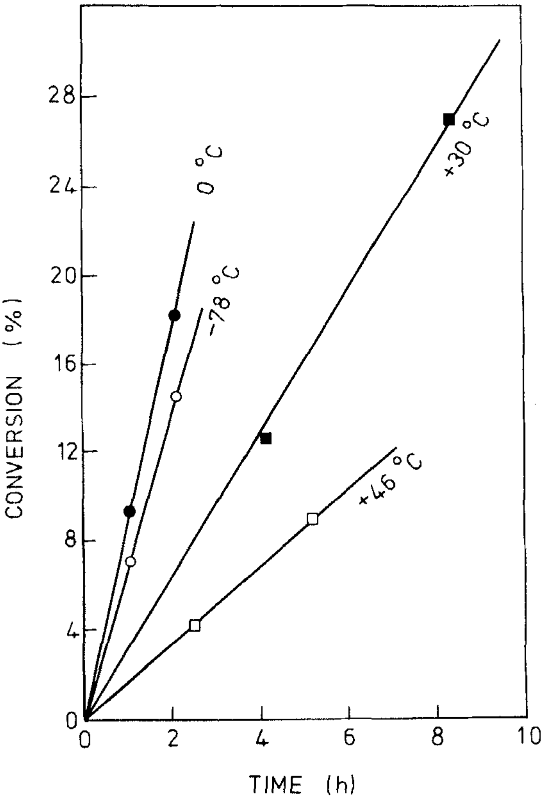


FIG. 6. Copolymer yield (conversion) as a function of irradiation time for various polymerization temperatures, comonomer compositions, and dose rates. (●) 0°C, x_{VC} = 0.72, I = 0.460 Mrd/h; (○) -78°C, x_{VC} = 0.50, I = 0.460 Mrd/h; (■) 30°C, x_{VC} = 0.76, I = 0.190 Mrd/h; (□) 46°C, x_{VC} = 0.88, I = 0.155 Mrd/h.

in agreement with the results of Schneider et al. [8] and have also been reported for the copolymerization of styrene with SO_2 [17].

Dose Rate Exponent

At a fixed temperature and comonomer composition the copolymerization rate R_p = constant × $[I]^m$, where I is the dose rate, the value of the dose-rate exponent m depending on the termination mechanism. Plots of log (R_p) versus log [I] are shown in Fig. 7. Neither

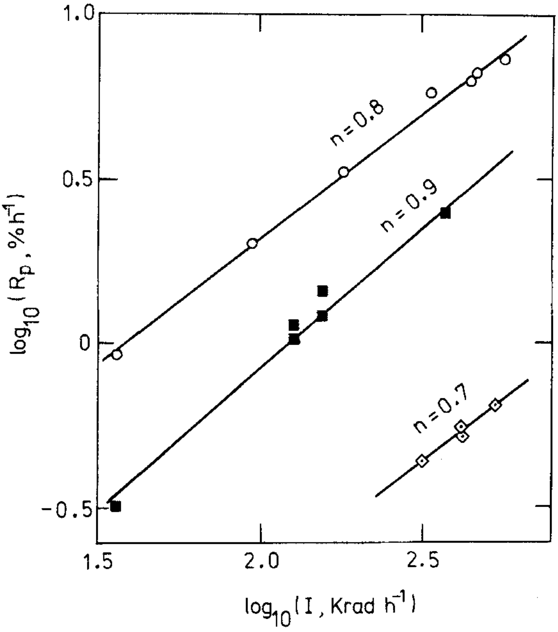


FIG. 7. Dose rate (I) dependence of copolymerization rate (R_p). (○) T_p = -78°C, x_{VC} = 0.5; (■) T_p = 46°C, x_{VC} = 0.8; (◈) T_p = 4.6°C, x_{VC} = 0.5.

comonomer composition nor copolymerization temperature had a significant effect on m, which was in the range 0.7 to 0.9 under these conditions.

Effects of Comonomer Composition and Polymerization Temperature

Comonomer mixtures in the range x_{VC} = 0.1 to 1.0 were copolymerized at six temperatures: -78, -45, -18, 0, 30, and 46°C. Figures 8 and 9 show R_p (at a dose rate of 0.42 Mrd/h) as a function of comonomer composition at each temperature. Conversions were kept sufficiently low that the change in comonomer composition was small, even at high temperatures and at concentration extremes. The copolymerization rates for three comonomer concentrations are plotted versus temperature in Fig. 10. The corresponding Arrhenius plots are shown in Fig. 11.

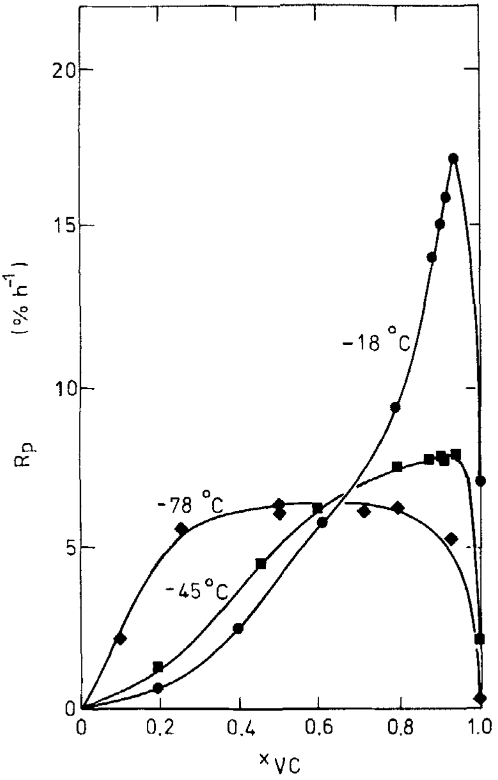


FIG. 8. Copolymerization rate (R_p) for radiation initiation as a function of comonomer composition at -78, -45, and -18°C [standard dose rate (I) = 0.421 Mrd/h].

Additives

Radical, anionic, and cationic species are produced by γ-irradiation. Thus cationic homopolymerization occurs concurrently with free radical copolymerization during irradiation of styrene-SO_2 mixtures [17, 18]. Although poly(vinyl chloride) is normally considered to be produced only by a free radical reaction, low molecular weight polymers have been produced by an ionic mechanism [19] which could also occur in SO_2. Therefore, selective scavengers were used to examine the role of free radical and ionic mechanisms during the copolymerization of vinyl chloride and SO_2 initiated by γ-irradiation. These experiments were particularly important because the copolymerization rate measurements indicated that a change in polymerization mechanism

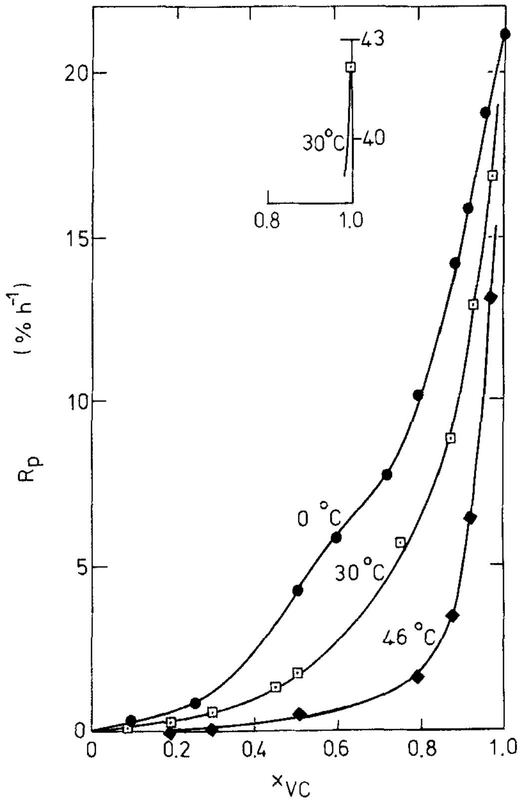


FIG. 9. Copolymerization rate (R_p) for radiation initiation as a function of comonomer composition at 0, 30, and 46° C [standard dose rate (I) = 0.421 Mrd/h].

occurred at 0° C between low- and high-temperature regions. This could be due to a change from ionic to free radical polymerization.

The rates of copolymerization at different temperatures and comonomer compositions in the presence of selective scavengers at a concentration of 10^{-3} mol/dm^3 are shown in Table 3. These results prove conclusively that the radiation-initiated copolymerization of VC and SO_2 is a free radical reaction at all temperatures and that no ionic homopolymerization occurs. Iodine is an efficient free-radical scavenger and in all cases completely inhibited copolymerization. Hydroquinone had only a retarding effect attributable to (1) limited solubility in the reaction mixture and (2) effective inhibition requiring the presence of oxygen [20]. Oxygen alone did not inhibit the

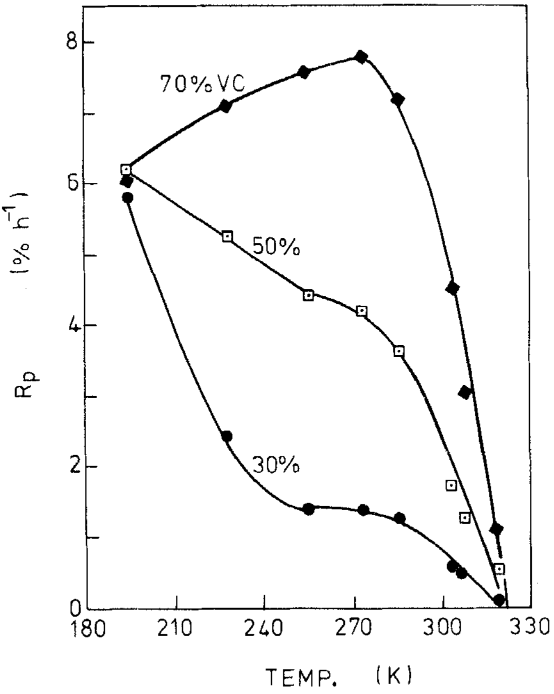


FIG. 10. Copolymerization rate (R_p) for radiation initiation as a function of polymerization temperature. (◆) x_{VC} = 0.70; (▣) x_{VC} = 0.50; (●) x_{VC} = 0.30.

copolymerization, which could be carried out in an open vessel with t-BuOOH initiation at low temperature. This was probably due to the inability of sulfonyl radicals to add oxygen [21] because of strong electrostatic repulsion. Acetone and DMF, which inhibit cationic polymerization [22], had no significant effect on the copolymerization rate. The rate was greater in the presence of CCl_4, which is known to act as a sensitizer for radiation-induced free radical polymerization due to the radiolytic production of $CCl_3^\bullet$ and $Cl^\bullet$ radicals with high G values.

Molecular Weights

[η]. The limiting viscosity numbers in THF at 25°C of copolymers with $\bar{n}$ = 4 and 16 prepared by radiation initiation at 30 and 46°C, respectively, were 56.0 and 54.6 cm^3/g. Approximate molecular

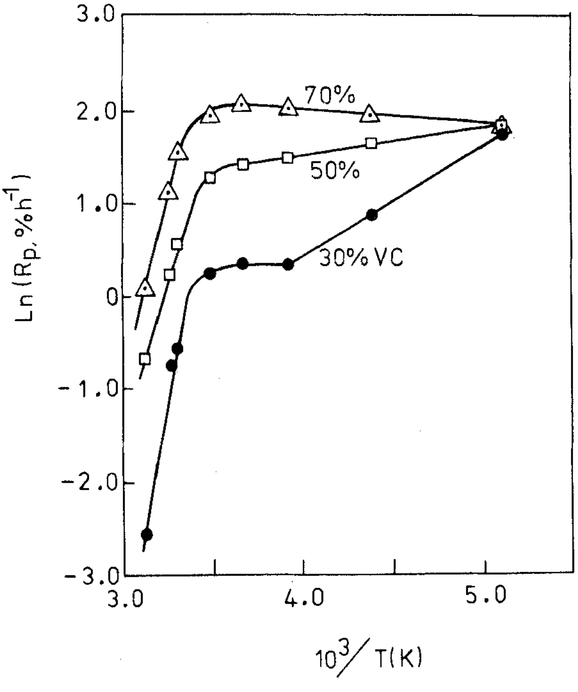


FIG. 11. Arrhenius rate plots for the comonomer compositions shown in Fig. 10.

weights can be obtained by using the constants $K = 49.8 \times 10^{-3}$ cm^3/g and a = 0.69 for PVC [23] in the Mark-Houwink equation, which gives $\overline{DP}_v \approx 400$ and $\overline{M}_v \approx 26{,}000$.

NMR. The ^{1}H NMR spectrum of a copolymer prepared by t-BuOOH initiation at -45°C is shown in Fig. 4. The sharp singlet at 1.8 ppm is attributed to t-BuO endgroups. The methyl protons of t-BuO groups usually resonate in the range 1.19 to 1.56 ppm [24] and the slight downfield shift of these protons in the copolymer probably indicates that the methyl group is γ to a sulfonyl unit, i.e., $(CH_3)_3C{-}O{-}SO_2{-}$. This is in accordance with the proposed radical intermediates formed in the t-BuOOH–SO_2 initiating system [25], leading to chain initiation by t-BuO–$SO_2^{\bullet}$.

The t-BuO groups observed in the ^{1}H NMR spectra are not due to occluded initiator, as copolymers prepared under the same conditions at -78°C did not show any measurable t-BuO resonance, due to their high molecular weight. The number of t-BuO groups per polymer molecule is not known and for the purposes of comparison we have assumed that it is one under all conditions. Table 4 gives the

TABLE 3. Effect of Several Additives on the Rate of Radiation-Induced Copolymerization R_p [standard dose rate (I) = 0.421 Mrd/h]: DMF = dimethylformamide, HQ = hydroquinone

Temperature (°C)	$(x_{VC})_m$	Additive (conc ≈ 10^{-3} mol/dm^3)	R_p (%/h)
30	0.52	-	1.36
		Acetone	1.30
		DMF	1.20
		HQ	0.21
		I_2	0.0
0	0.52	-	3.44
		Acetone	3.65
		DMF	3.73
		HQ	0.38
		I_2	0.0
		CCl_4	9.70
	0.81	-	9.07
		Acetone	8.71
		DMF	8.95
		HQ	2.72
		I_2	0.0
-78	0.22	-	5.61
		Acetone	4.94
		DMF	6.13
		HQ	0.44
		I_2	0.0
	0.80	-	6.32
		Acetone	5.53
		DMF	5.84
		HQ	5.52
		I_2	0.0

TABLE 4. Degrees of Copolymerization and Molecular Weights of Polymers Prepared by Chemical Initiation Calculated from NMR Spectra

Temperature (°C)	$(x_{VC})_m$	n	$\overline{DP}_n$	$\overline{M}_n/10^3$
-78	0.4	1.79	69	4.3
-45	0.2	1.20	125	7.9
	0.8	1.60	1182	74.6
-18	0.2	1.64	47	2.9
	0.4	1.80	126	8.0
	0.6	1.90	274	17.3
	0.8	1.95	583	36.7

number-average degree of polymerization $\overline{DP}_n$ and molecular weight $\overline{M}_n$ calculated on this basis. The upper limit of $\overline{M}_n$ measurable from the t-BuO PMR peak was 40,000 and samples prepared at -78 and -95°C had $\overline{M}_n$ in excess of this. Copolymer solubilities also supported qualitatively the marked trends of higher molecular weights at low temperatures and high VC content in the comonomer mixture.

Composition of Copolymer

The average macroscopic composition of the copolymers, expressed as mole fraction of vinyl chloride $(\overline{x}_{VC})_p$ and $\overline{n}$ value, is shown as a function of comonomer composition for each of the polymerization temperatures studied (-95, -78, -45, -18, 0, 30, and 46°C) in Fig. 12. The average comonomer composition $(\overline{x}_{VC})_m$ is the arithmetic mean of the initial and final compositions, and the compositions of samples prepared below 0°C are corrected to the true $\overline{n}$ value (= x + y) to allow for dehydrochlorination when this occurred.

The main characteristics of the copolymer/comonomer composition relationships are the progressive increase in $\overline{n}$ with increasing polymerization temperature over the complete liquid-phase copolymerization range and the relatively small dependence of $\overline{n}$ on comonomer composition below $x_{VC} = 0.8$. This is particularly evident at $T_p = 0°$. However, the vinyl chloride content of the copolymer increased markedly for higher x_{VC} values.

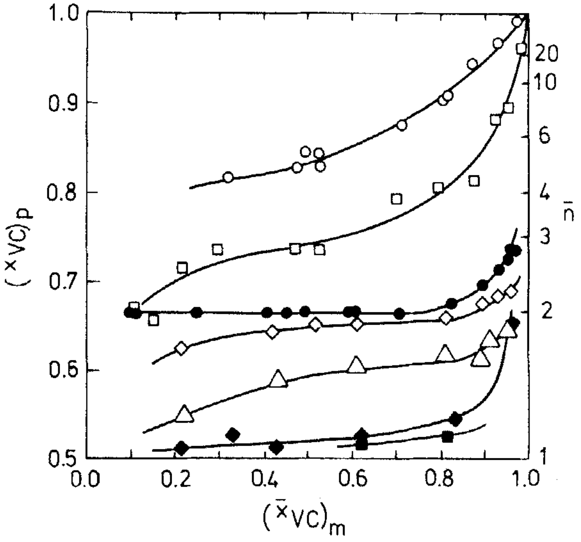


FIG. 12. Copolymer composition versus comonomer composition relationships for various polymerization temperatures. Compositions corrected for dehydrochlorination where necessary ($\bar{n} < 2$). (○) 46, (□) 30, (●) 0, (◇) -18, (△) -45, (◆) -78, (■) -95°C.

Dilution Effects

Figure 13 shows the effect on the copolymer composition at several temperatures of varying dilution of a fixed VC:SO_2 comonomer composition (VC:SO_2 $\approx$ 1.0) in CCl_4, methanol, and dichloromethane, and Fig. 14 shows the effect on the number-average fraction N(1) of single VC sequence, i.e., VC units in SVS triads, determined by ^1H NMR [12]. At -78°C there is apparently a slight increase in $\bar{n}$ on dilution in CH_2Cl_2, but a substantial increase on dilution in CH_3OH, indicating that the latter is not an "inert" diluent. Methanol forms a fairly strong association complex with SO_2 (K_x = 2.37 at 23.1°C) [26] and the observed dilution effect with this solvent can be attributed to the removal of "free" SO_2 by complexation, so that the effective comonomer composition (VC:SO_2) is changed.

At -18°C the vinyl chloride content of the copolymer increased slightly, but significantly, on dilution (from $\bar{n} < 2.0$ to $\bar{n} > 2.0$) accompanied by a remarkable decrease to zero of the proportion of SVS sequences. The vinyl chloride content of the copolymer also increased slightly on dilution at 0°C and markedly at 30°C.

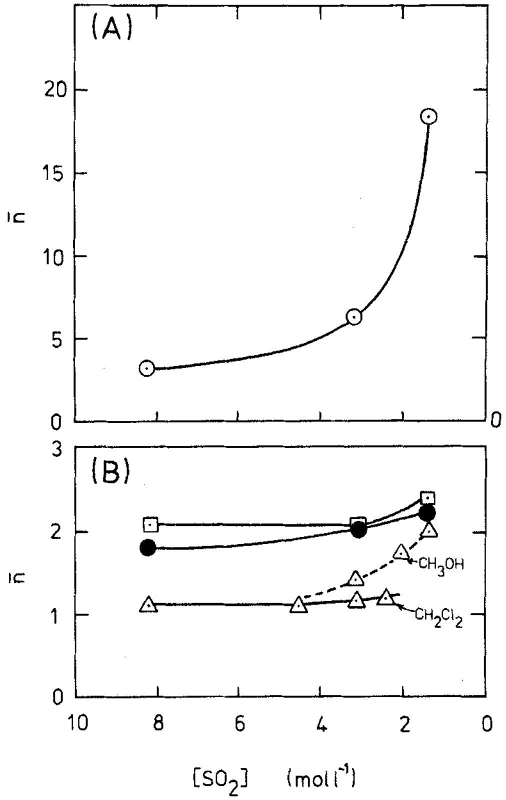


FIG. 13. Dilution effect on copolymer composition (CCl_4 diluent except where indicated). (◉) 30°C, (▣) 0°C, (●) -18°C, (▲) -78°C.

DISCUSSION

Copolymer Composition

Our measurements have provided experimental copolymer/comonomer composition relationships at seven temperatures covering the complete range for the liquid-phase copolymerization of vinyl chloride with sulfur dioxide (Fig. 12). We have studied particularly comonomer mixtures with high vinyl chloride contents ($x_{VC} > 0.8$), as results in this composition region are essential for quantitative comparison with models for the copolymerization.

Copolymer compositions corresponding to comonomer mixtures

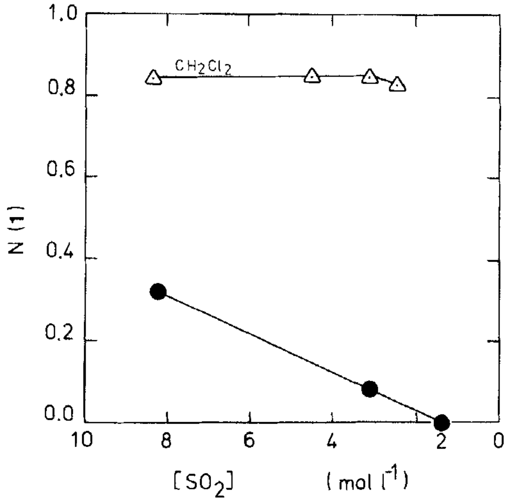


FIG. 14. Dilution effect on copolymer sequence distribution. N(1) = proportion of SVS sequences. (●) -18 °C, (▲) -78° C.

with $x_{VC} < 0.2$ are difficult to obtain and less reliable due to the very low rates above -78° C for radiation initiation (Figs. 8 and 9) and the consequent degradation of the copolymer by the high dose required for a reasonable yield. At -78 and -95° C radiation-induced dehydrochlorination was rapid, and high x_{SO_2} comonomer mixtures were solids. Copolymerization by chemical initiation with t-BuOOH/CH_3OH was slow at -45 and -18° C and negligible at higher temperatures. Therefore, Fig. 12 contains only a few results for $x_{VC} < 0.2$. The behavior at both extremes of the comonomer composition range is important for distinguishing the mechanism of copolymerization. We deduce from Fig. 12 that the copolymer composition approaches $\bar{n} = 1.0$ as $x_{VC} \rightarrow 0$ for polymerization temperatures below 0° C. At 0° C the copolymer composition is $\bar{n} \approx 2.0$ for $x_{VC} = 0.1$ to 0.8. We propose that the copolymer composition approaches $\bar{n} = 2.0$ as $x_{VC} \rightarrow 0$ for polymerization temperatures $> 0°$ C. Thus the macroscopic copolymer compositions indicate that the copolymerization behavior is divided into two temperature regions. This is supported by the rates of copolymerization and the microstructure of the copolymers [12].

We have compared our copolymer/comonomer composition relationships with the results of Schneider, Denaxas, and Hummel [8]

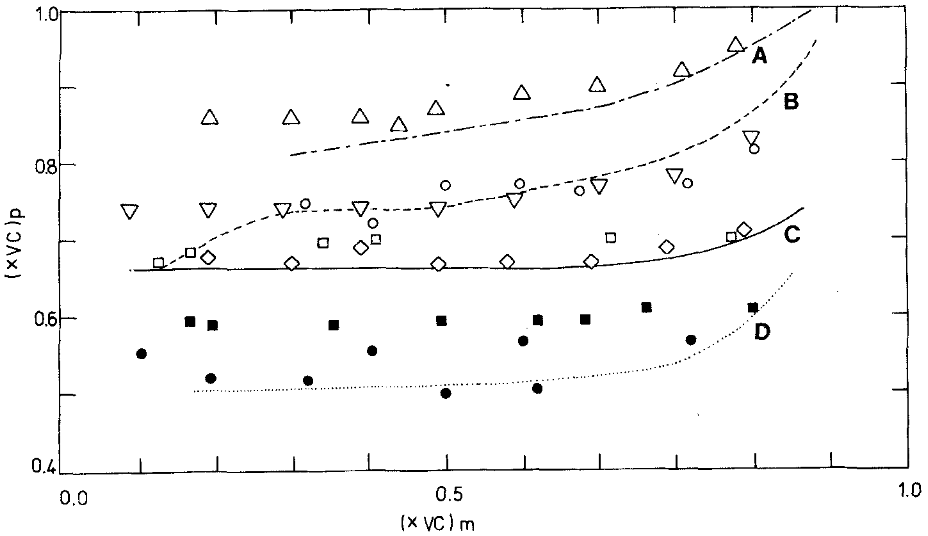


FIG. 15. Literature values for composition of poly(vinyl chloride sulfone) as a function of comonomer composition. A (△): Matsuda and Thoi [14] at 50°C; (– -): present work at 46°C. B (○): Suzuki et al. [9] at room temperature; (□): Schneider et al. [8] at 20°C; (▽): Matsuda and Thoi [14] at 28°C; (--): present work at 30°C. C (◇): Matsuda and Thoi [14] at 0°C; (—): present work at 0°C. D (●): Suzuki et al. [9] at -78°C; (■); Schneider et al. [8] at -75°C; (· ·): *present work at -78°C.*

and Suzuki, Ito, and Kuri [9] in Fig. 15. Our results at 30°C are similar to those of Suzuki et al. at room temperature. They did not specify this temperature, but we deduce from their Fig. 7 that it is about 20°C. Therefore, their results are significantly higher than ours, whereas those of Schneider et al. are significantly lower and in particular do not show the variation with comonomer composition. At -78°C the results of Suzuki et al. show a large variability, giving average values of $\bar{n}$ slightly higher than ours. Schneider et al. have reported appreciably higher values. We attribute these discrepancies to their use of microanalysis figures for sulfur, which will give erroneously high values of $\bar{n}$ if dehydrochlorination has occurred. We have shown that dehydrochlorination is a feature of radiation-initiated polymerization below 0°C [12]. Our results for the copolymer compositions are reliable, particularly at -78°C, as they are based on the ^{1}H NMR analytical technique which enables quantitative evaluation of the proportion of dehydrochlorinated vinyl chloride units.

Our copolymer compositions for $T_p \geq 0°C$ are also compared with the recent results of Matsuda and Thoi [14] in Fig. 15. The agreement is good, confirming that the method of initiation (γ-irradiation compared with cumene hydroperoxide and AIBN) does not affect the copolymer composition in this temperature range.

Copolymerization Rate

Our copolymerization rate versus comonomer composition relationships for radiation initiation at different temperatures (Fig. 8 and 9) are basically similar to those of Suzuki et al., but show appreciable quantitative differences. At high temperatures R_p increases approximately exponentially with x_{VC} and at low temperatures shows a maximum near $x_{VC} = 0.5$. The maximum results from the low rate of homopropagation of vinyl chloride at these temperatures. At -45°C the maximum rate occurred at high x_{VC}, and this became exceptionally pronounced at -18°C.

We attribute the accelerating effect of a small proportion of SO_2 (< 5 mol %) on the rate at -45 and -18°C to scavenging of VC radicals by SO_2 at these temperatures, according to

(a) $CH_2{=}CHCl \rightsquigarrow R.\ (H^{\bullet},\ Cl^{\bullet},\ CH_2{=}CH^{\bullet})$

(b) in the absence of SO_2:

$$R^{\bullet} + V \rightarrow RV^{\bullet} \qquad \text{(i)}$$

$$RV^{\bullet} + V \rightarrow RVV^{\bullet} \qquad \text{(ii)}$$

$$2RV^{\bullet} \rightarrow \text{low molecular weight product} \qquad \text{(iii)}$$

(c) in the presence of SO_2:

$$RV^{\bullet} + S \rightarrow RVS^{\bullet} \qquad \text{(iv)}$$

$$2RVS^{\bullet} \not\rightarrow \qquad \text{(v)}$$

$$RVS^{\bullet} + V \rightarrow RVSV^{\bullet} \qquad \text{(vi)}$$

In the absence of SO_2, Step (iii) will compete with the homopropagation Step (ii), which is slow at low temperatures. However, SO_2, when present, will rapidly scavenge these radicals by Step (iv), forming sulfonyl radicals which cannot terminate, so chain propagation to form copolymer is now favored. At higher temperatures, the rate of (ii) will increase relative to (iii), Step (iv) and Step (vi) become reversible and SO_2 exhibits a retarding effect.

Chemical Initiation

Many chemical initiators are ineffective for the vinyl chloride-SO_2 system. We have shown that the redox system of t-BuOOH and methanol, in the presence of SO_2, gives high rates of copolymerization at -95 and -78°C, but the rate decreases to nearly zero for $T_p > 18°$. Marvel [5] was able to obtain high rates at 0° by using large quantities of peracetic acid and we have repeated this. Suzuki et al. [24] have reported the preparation of poly(vinyl chloride sulfone) with $\bar{n} > 2.5$ at 30°C using diisopropyl peroxydicarbonate as initiator.

Matsuda and Thoi [14] have reported the variation in the rate of copolymerization across the composition range for undiluted comonomer mixtures only for 28°C; these were very low and increased linearly with x_{VC}. The much more rapid increase in R_p with x_{VC} shown in Fig. 9 for radiation-induced copolymerization can be attributed, at least in part, to the higher $G(R^\cdot)$ in VC compared with SO_2. The increase in R_p with x_{SO_2} for initiation with t-BuOOH/MeOH shown in Table 2 is evidently the result of enhanced radical production from the redox reaction between t-BuOOH and SO_2 with increasing SO_2 concentration.

Kinetic Aspects

Initiation

R_p depends on the initiation, propagation, and termination reactions. The rate of radiation initiation is

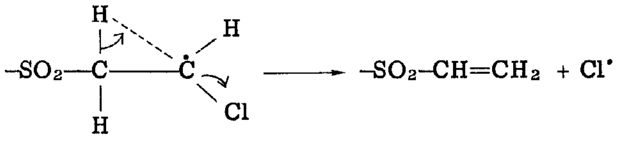
$$R_i = I(G_V[V] + G_s[S])$$

where G_V and G_s are the radiation chemical yields of initiating radicals from VC and SO_2, respectively, and I is the radiation dose rate. $G(R^\cdot)$ for bulk VC = 8.6 [27] and for SO_2 = 1.35 [28]. Therefore, R_i will increase sixfold over the comonomer composition range if these values are applicable to VC-SO_2 mixtures, and this may account for the greater increase in R_p with x_{VC} shown in Fig. 9 than was observed by Matsuda and Thoi [14]. G(R$^\cdot$) is usually independent of the irradiation temperature in the liquid phase.

Termination

Bimolecular termination in radiation-initiated polymerization will give m = 0.5 in the relationship $R_p = kI^m$, whereas linear termination will give m = 1.0. The value of 0.7 to 0.9 found in the present work indicates that both types of termination occur. This is in contrast to radiation-initiated homopolymerization of vinyl chloride [29, 30] and copolymerization of styrene with sulfur dioxide [18, 31, 32], where m ≈ 0.5. Suzuki et al. [9] stated that m = 1 for the radiation-initiated copolymerization of vinyl chloride with sulfur dioxide at -78 and 20° C.

In the homopolymerization of vinyl chloride, termination is predominantly by disproportionation [33, 34] and the molecular weight is controlled by chain transfer to the β-hydrogen [35]. We have observed that poly(vinyl chloride sulfone) had a significantly higher molecular weight when prepared (-45° C, $x_{VC} = 0.40$) from vinyl chloride-β,β-d_2 compared with the fully protonated monomer (determined from the t-BuO resonance in the ^{1}H NMR spectrum). This suggests that scission of a methylene C–H bond must be a step in the termination. A possible mechanism would be



The sulfonyl group is known to activate hydrogen atoms in the α-sulfonyl position, and this was confirmed for poly(vinyl chloride sulfone) by (1) H/D exchange in D_2O/DMSO solutions and (2) dehydrochlorination with H loss from the α-sulfonyl position. Styrene does not have a readily eliminated substituent, hence the termination would be expected to be bimolecular, giving m = 0.5 for copolymerization with SO_2, as in its homopolymerization.

CONCLUSIONS

1. Infrared spectroscopy provides a convenient analytical method for poly(vinyl chloride sulfone) when VC:SO_2 = $\bar{n} > 2$ by comparison of the absorbances due to the CH_2 bending and SO_2 symmetrical stretching vibrations at 1423 and 1140 cm^{-1}, respectively.

2. The ^1H NMR spectrum of poly(vinyl chloride sulfone) enables an accurate, quantitative analysis of the composition of the copolymer, including the extent of dehydrochlorination. Molecular weights can be estimated from the t-BuO resonance at 1.8 ppm for copolymers prepared by t-BuOOH initiation.

3. The relationships between macroscopic copolymer composition and comonomer composition for temperatures between -95 and -46°C show that

(a) The copolymer composition is $\bar{n} \approx 2.0$ at 0°C for $x_{VC} = 0.1$ to 0.8.
(b) $\bar{n}$ increases with increasing x_{VC} above $x_{VC} = 0.8$ at all temperatures.
(c) The limiting composition as $x_{VC} \to 0$ was $\bar{n} = 1.0$ for $T_p < 0°C$ and $\bar{n} = 2.0$ for $T_p > 0°C$.

4. A marked effect of dilution with an inert solvent on $\bar{n}$ was observed at +30°C and on N(1) = number fraction of single VC sequences at -18°C. Smaller dilution effects were observed at other temperatures.

5. The variation in R_p with temperature and comonomer composition indicated two temperature regions with an apparent change in mechanism at 0°C.

6. The rate of formation of high-molecular weight copolymer, or vinyl chloride homopolymer, was near zero on irradiation of comonomer mixtures above ≈55°C.

7. SO_2 had a very strong retarding effect on the polymerization for $T_p \geq 0°C$.

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