of interpretation have been pointed out above, and in fact seem responsible for the differences observed. In general, where this can be checked, the molecular weight of the base polymer appears to have been close to or less than M_c at the particular concentration used. This must lead to low values of viscosity increase on association. For instance, the isoprene-capped polystyrenes[6] were either used at $v = 0.14$, $M = 260{,}000$ or $v = 0.30$, $M = 139{,}000$. M_c is 320,000 or 150,000, respectively, under these conditions. Molecular weights at least 100,000 above M_c are necessary before the 3.4 law becomes accurate for styrene. Similar conditions seem to have been used for polyisoprenyllithium itself in benzene. With polyisoprene the critical molecular weights at a given volume fraction are lower than with polystyrene solutions, and it is easier to attain the region of validity of 3.4 law. Nevertheless, the original data[17] suggest that a volume fraction of 0.16 was used for two polymers of $M = 80{,}000$ after killing. The value of M_c at this concentration is 88,000.[18] Two other polymers were used at a volume fraction of 0.26 where M_c will be 54,000; their molecular weights were ~74,000 and ~110,000. These two polymers gave 13-fold and 15-fold changes in viscosity, respectively, between the isoprene-capped and terminated polymers, whereas the first two gave 10-fold increases. Clearly, although the latter two experiments were dismissed as being caused by experimental error, what was really observed was an increase in the viscosity ratio as conditions approached the region of validity of the 3.4-power law. In fact, a 15-fold change of viscosity was observed by us under appropriate experimental conditions (Table IV). This is approximately what would be expected for fourfold association. We cannot be exact about this because we have presently no data on four-star polyisoprenes, but we suppose that the difference in viscosity of four-star polyisoprenes compared to linear polymers is about the same as for polystyrenes.

The light-scattering measurements indicating an association number of two for polyisoprenyllithium were made in *n*-hexane.[6] We have shown that in the similar good solvent for polyisoprene, cyclohexane, extrapolation to zero concentration based on three points is a hazardous procedure, for the line is strongly curved due to partial dissociation (Figure 2). Lower concentrations of active centers are used in light-scattering measurements (down to 10^{-5} *M*, where the association number is about three). Owing to the changing association number in the concentration range, a meaningful analysis of the results cannot be obtained in a good solvent. Measurements on isoprenyllithium-capped polystyrene in cyclohexane are required to solve this problem.

In summary, we have presented evidence for twofold association of polystyryllithium and fourfold association for polybutadienyl and polyisoprenyllithium. The latter compound dissociates on dilution but does not reach an association number of two at the lowest usable concentrations (~10^{-5} *M*). The difficulties in using concentrated solution viscosities as a diagnostic tool have been assessed. Without an exact knowledge of the decrease in viscosities of branched polymers compared to linear ones, accurate measurements of association numbers are not obtainable with this technique. The expected accuracy of the method is much lower than expected from simple use of the 3.4-power law. It is difficult to keep in the range of applicability of this law in conventional anionic systems.

Acknowledgment. We are indebted to Dr. J. Prud'homme for the data presented in Figure 2 which was obtained during the tenure of a postdoctoral fellowship at N.R.C.

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Structural Control in the γ-Radiation-Initiated Polymerization of 1-Vinyluracil[1]

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ABSTRACT: Poly(1-vinyluracil) has now been prepared with complete repression of cyclopolymerization *via* γ-radiation-initiated polymerization using the following techniques: (a) polymerization at low temperature, (b) polymerization at high concentrations of monomer, (c) polymerization in the solid state, (d) polymerization of negatively charged monomers, and (e) polymerization of monomers containing bulky substituents. As the temperature was reduced from 0 to −78° the extent of cyclopolymerizations decreased from 20% to 0% in solution. At 0°, high concentrations of negatively charged 1-vinyluracil also led to 0% cyclopolymerization. In the solid state, polymerization occurred at 40° without any cyclopolymerization. At very high doses, some cross-linking was observed. Polymerization of 6-methyl-1-vinyluracil at 25° in solution led to the completely noncyclopolymerized polymer. The polymers were amorphous by X-ray diffraction, and the 100-MHz nmr spectra at 170° in DMSO-d_6 suggested that the poly(1-vinyluracils) varied in their degree of syndiotacticity. The ultraviolet hypochromism at 264 mμ was found to vary widely with the tacticity.

In a previous report from this laboratory it was shown that the free-radical-initiated polymerization of 1-vinyluracil (I) led to a poymer which contained a high percentage of cyclopolymerizated units in the main chain.[4] Although we,[5]

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(2) To whom inquiries should be addressed.

(3) In partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Texas A&M University.

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Table I
Polymerization of 1-Vinyluracil and 6-Methyl-1-vinyluracil

Monomer	Expt	Solvent	Concn, %	Dose rate r, hr × 10^{-5}	Temp, °C	Time, hr	Yield, %	Uv[a] λ_{max}	Uv[a] ϵ	% uracil by nmr	$\eta_{sp}{}^{b}/c$
1-VU	1	20% NH_4OH	17	2.52	0	14.5	83	264	4740	80	0.31
	2	50% NH_4OH	3.5	4.07	−78	117	78.2	264	5180	100	
	3	Liquid NH_3	15	4.07	−78	14	35	264	4950	100	0.23
	4	2 *M* NAOH	15	4.07	0	6	58			98	
	5	7 *M* NaOH	45	4.07	0	0.5	17	264	4060	100	0.82
	6	7 *M* NaOH	45	4.07	0	3	30[c]	264	4860		
	7	7 *M* NaOH	45	4.07	−78	6	18.6[c]	264	4280	92.2	0.75
	8	7 *M* NaOH	22	4.07	−190	0.16	6				
	9	Solid state		4.07	40	94	15.5	264	3440	100	0.27
	10	Solid state		4.07	40	240	2.66[c]				
6-MVU	11	H_2O	10	2.52	25	6	36	267	8590	100	0.36
	12	H_2O	10	2.52	0	6	10			100	

[a] At pH 12, 0.2 *M* KCl, 0.2 *M* NaOH. [b] c = 0.5 g/dl in DMSO. [c] Some cross-linking.

as well as others,[6–9] have been interested in studying the physicochemical and biochemical properties of vinyl polymer analogs of the nucleic acids, the presence of cyclopolymerized units in poly(1-vinyluracil) would make any interpretation of its properties, complicated as dihydrouracil rings do not base pair and stack very well.[10] Even the presence of a relatively low percentage of cyclopolymerized units in the polymer would be expected to create enough defects to seriously impair its base pairing with complementary macromolecules and its potential biochemical template surface.

We now wish to report on the preparation of noncyclopolymerized poly(1-vinyluracil) (PVU).

Results and Discussion

All attempts to prepare stereoregular noncyclopolymerized PVU by cationic and heterogeneous[11] catalysis failed. Because of this we focused our attention on the γ-radiation-initiated[12,13] polymerization of I under special conditions which would not be expected to lead to cyclopolymerization. The ratio of the rate of cyclopolymerization (R_c) to the ratio of normal propagation (R_p) can be assumed to be described by the following simplified equations

$$\frac{R_c}{R_p} = \frac{k_c}{k_p[\mathrm{m}]} = \frac{A_c e^{-(E_c - E_p)/RT}}{A_p[\mathrm{m}]}$$

where k_c and k_p are the rate constants for cyclopolymerization and propagation, [m] = monomer concentration, E_c and E_p are the activation energies for cyclopolymerization and propagation, and $E_c > E_p$.[14] Guided by the above equation it was found that using some of the following techniques and combinations thereof, cyclopolymerization could be completely repressed: (a) polymerization at low temperature, (b) polymerization at high concentration of monomer, (c) polymerization in the solid state, (d) polymerization of negatively charged monomers, and (e) polymerization of monomers containing bulky substituents.

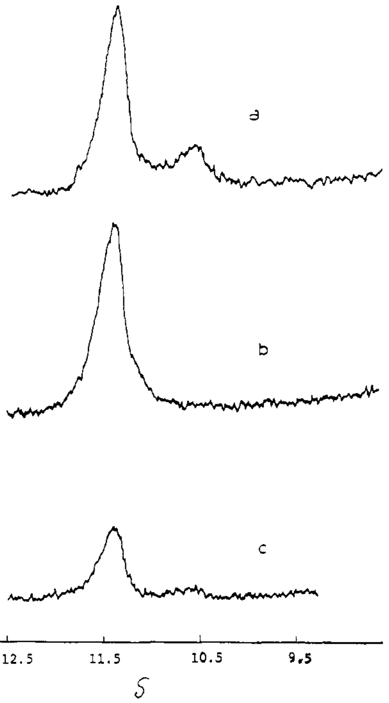

Figure 1. Nuclear magnetic resonance spectra of N–H protons in DMSO-d_6 in the δ 9.5–12.5 range at 25° relative to TMS: (a) NH_4OH, 0°; (b) NH_3(l), −78°; (c) 7 *M* NaOH, −78°.

Low-Temperature Polymerization in Ammonia Solutions. It has been reported for other cyclopolymerizable monomers that as the temperature of polymerization is reduced the percentage of cyclized units decreases.[14] In the γ-radiation-initiated polymerization of I in aqueous ammonia solutions it was found that as the temperature was lowered from 0 to −78° the per cent cyclopolymerization decreased from 20 to 0%. Liquid ammonia at −78° was an even more convenient solvent because higher concentrations of monomer could be obtained (Table I, experiments 1, 2, 3). In these experiments, and others to follow, the per cent uracil in the polymers was determined from the nuclear magnetic resonance spectra[4] by integration of the uracil N–H proton at δ 11.44. The chemical shift for the cyclo N–H proton is at δ 10.62. The spectra in the N–H region for these polymers are shown in Figure 1a,b. The infrared spectrum was the

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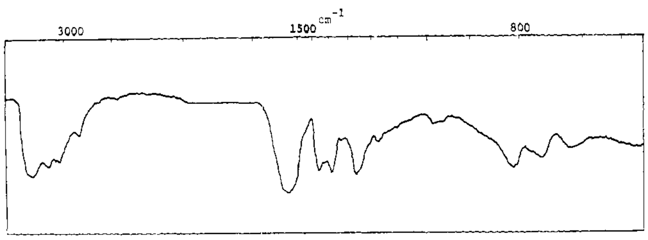

Figure 2. Infrared spectrum of solid state PVU in KBr.

same as that presented in Figure 2. A typical nuclear magnetic resonance spectrum at 170° in DMSO-d_6 for noncyclopolymerized PVU is shown in Figure 3. The uracil 5 and 6 protons are seen to occur at δ 5.65 and 7.38, respectively, while the methine proton occurs at the low-field value of δ 4.26 because of the magnetic anisotropy of the 2 position carbonyl group. The peak at δ 2.65 is due to DMSO-d_5, while the methylene absorption can be seen to occur at δ 2.25. The integration of all protons was consistent with the structure.

Polymerization in 7 *M* Sodium Hydroxide. Sodium hydroxide (7 *M*) has been found to be an excellent solvent for I. At 0° this system becomes a highly viscous liquid. The very high concentrations of monomer which could be obtained allowed us to take advantage of the decrease in cyclopolymerization with increase in monomer concentration.[15] Furthermore, I became negatively charged in this solvent due to the acidic N–H proton of the uracil ring, and this was expected to decrease the extent of cyclopolymerization because of electrostatic repulsion between the penultimate and growing chain end uracils. Indeed, γ-radiation-initiated polymerization at 0° led to pure noncyclopolymerized poly(1 vinyluracil) (Table I, experiment 5). Extremely rapid rates of polymerization were observed in this solvent, probably because the termination rate constant was decreased in the viscous media.[16] The nuclear magnetic resonance spectrum at 170° was similar to that obtained from experiment 3.

When the irradiation was carried out at 0° for more than 3 hr, increasing amounts of cross-linked polymer were formed. (Table I, experiment 6). At $-78°$, the 7 *M* sodium hydroxide solution became a rigid glass and polymerization led to either 7.8% cyclopolymerization or free-radical attack on the uracil rings along with some cross-linked material (Table experiment 7) (see Figure 1c). This was a surprising result in light of our low-temperature experiments in ammonia solutions. Possibly the rigidity of the glass decreases the diffusion of the adding monomers, thereby allowing cyclopolymerization to compete. On the other hand, we have not ruled out the possibility of dimerization and addition of hydrated electrons or other primary free radicals to the 5,6 double bond of the uracil rings[13,17] under these conditions. It is important to emphasize here that none of these processes were observed in the other experiments.

Solid-State Polymerization. Topotactic control in solid-state polymerizations has been demonstrated previously.[18,19] The polymerization of I in the solid state at 40° for 4 days led to pure PVU with the complete absence of any cyclopolymerization (Table I, experiment 9). As reported for 1-methyluracil,[20] I probably exists in the solid state as hydrogen-bonded dimers. The rigid orientation of the rings in the crystal may have prevented the penultimate and growing chain end uracils to be in the proper conformation for cyclopolymerization.[4] The dimeric crystal structure of 1-methyluracil is shown in Figure 4.

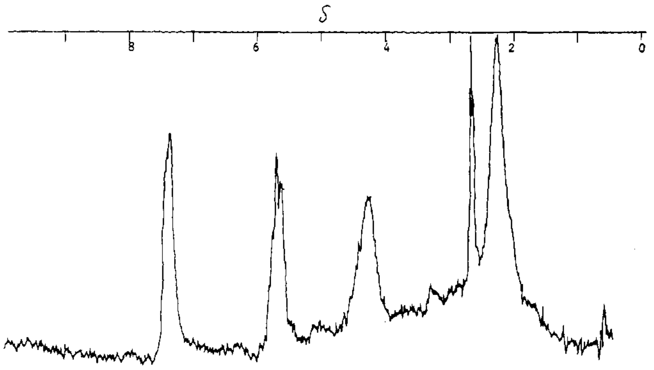

Figure 3. Nuclear magnetic resonance spectrum of solid-state PVU at 170° in DMSO-d_6.

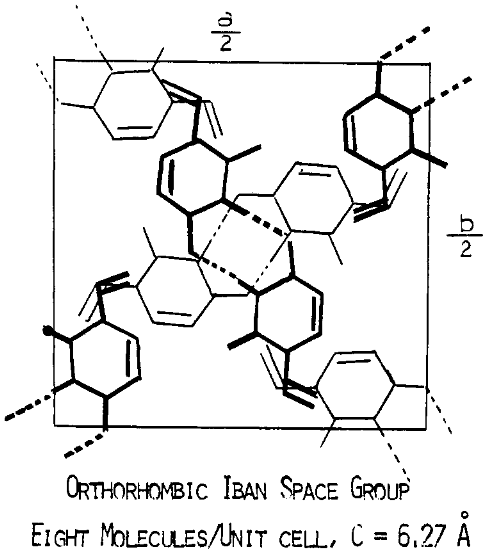

Figure 4. Unit cell of 1-methyluracil with vinyl groups replacing methyls.

Although carried out at higher temperatures, the solid-state polymerization was much slower than the $-78°$ polymerization in liquid ammonia. At much higher doses of γ radiation, lower yields and cross-linking were observed (Table I, experiment 10). The nuclear magnetic resonance spectrum of the polymer obtained in experiment 9 at 170° is shown in Figure 3 and the infrared spectrum is shown in Figure 2.

Polymerization of 6-Methyl-1-vinyluracil. 6-Methyl-1-vinyluracil was not expected to cyclopolymerize as readily as I because models indicated that the 6-methyl groups would sterically inhibit the proper orientation of the rings for cyclopolymerization. The monomer was prepared by the general *N*-vinylation reaction reported elsewhere.[21] 6-Methyluracil was first converted into its bis(trimethylsilyl) derivative by reaction with hexamethyldisilazane,[22] and then it was

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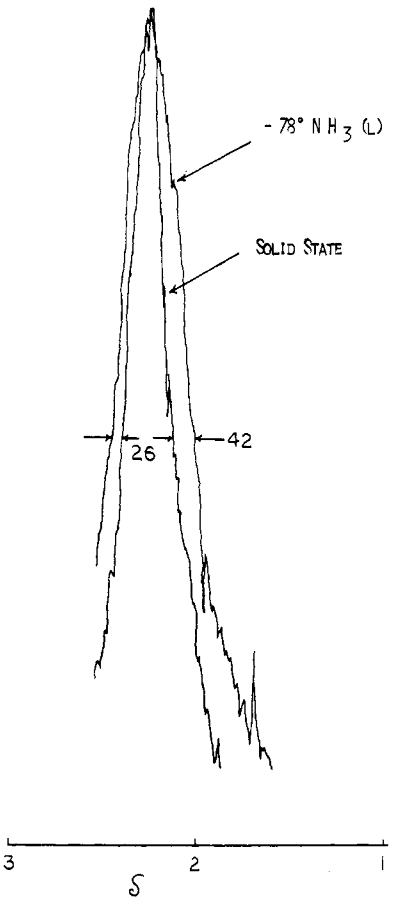
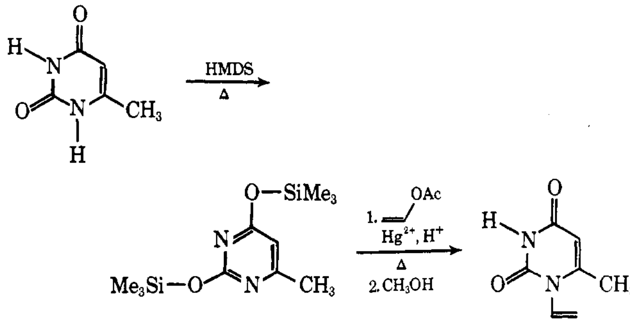


Figure 5. Nuclear magnetic resonance methylene signals of solid-state PVU and −78° liquid ammonia PVU at 170° in DMSO-d_6.

N-vinylated with mercuric acetate and vinyl acetate. This latter reaction proceeded more slowly than the vinylation of 2,4-bis(trimethylsilyl)uracil because of steric hindrance by the additional methyl group.



As expected, γ-radiation-initated polymerization in water at 0 and 25° led to poly(6-methyl-1-vinyluracil), with the complete absence of cyclopolymerized units (Table I, experiment 11 and 12).

Tacticity of PVU. As a general rule, free-radical polymerizations of vinyl monomers have been found to lead to highly syndiotactic polymers.[23] It is therefore reasonable to assume that the −78° solution polymerization of I led to a predominantly syndiotactic PVU. The polymerization of the negatively charged I at 0° is also expected to lead to a syndiotactic polymer because of electrostatic repulsion between the adding monomer and the growing chain end. The methylene signals observed at δ 2.25 in the high-temperature nuclear magnetic resonance spectra of the polymers prepared in experiments 3 and 5 had half-widths of 42 Hz and were not sufficiently resolved to determine the syndiotacticity.[24] The solid-state polymer (experiment 9), however, had a very sharp methylene signal with a half-width of only 26 Hz, and this suggested that this PVU was very highly syndiotactic. A comparison of the methylene signals at 170° can be seen in Figure 5.

As already mentioned, it has been reported that 1-methyluracil[20] crystallizes with an orthorhombic *Iban* space group and that the methyl groups are all aligned 3.13 Å apart parallel to the C axis. If by chance I crystallizes with similar packing, then free-radical propagation along the C axis would be expected to result in syndiotactic addition. This can be seen in Figure 4, where vinly groups have been drawn into replace the methyls. If I does indeed crystallize like 1-methyluracil, then the *a* and *b* unit cell dimension would probably be larger than shown to accommodate the additional atoms of the vinyl groups. In the unit cell drawn, it seems highly unlikely that the geometry would allow polymerization to take place in the *ab* plane.

In Table I it can be seen that the ultraviolet extinction coefficients cannot be correlated with low degrees of cyclopolymerization. It seems likely that the decrease in absorption due to cyclopolymerization is being compensated for by a decrease in hypochromism resulting from destacking. Even the extinction coefficients for the noncyclopolymerized polymers varied widely. The solid-state PVU had the lowest extinction coefficient corresponding to 51% hypochromism,[25] while the PVU prepared in liquid ammonia at −78° exhibited 29% hypochromism. Evidently, this can probably be attributed to the differences in tacticity.

All of the PVU's including the solid-state polymer were found to be amorphous by X-ray diffraction, but this might be a result of the random rotational orientations of the uracil rings along the backbone.

Experimental Section

General. Ultraviolet, infrared, and nuclear magnetic resonance measurements were carried out as previously reported, except that octamethyltetrasiloxane was used as an external standard.[4] A 25,000-Ci cobalt-60 source was used for the radiation experiments, and dose rates were determined with the Frick dosimeter.[26]

6-Methyl-1-vinyluracil. The general procedure of Kaye and Chang was used.[21] 6-Methyluracil (8 g, 0.063 mol) was heated at 145–150° with hexamethyl disilazane (20 ml) and a trace of ammonium sulfate for 24 hr, at which time a clear solution remained. Distillation of the mixture through a 6-in. Vigreaux under reduced pressure afforded 4.5 g (26.5%) of 2,4-bis(trimethylsilyl)-6-methyluracil, which crystallized in the receiver: mp 72.5–74°, bp 97° (2.7 mm). 2,4-Bis(trimethylsilyl)-6-methyluracil (3 g, 0.011 mol) was refluxed with dry vinyl acetate (30 ml), mercuric acetate (0.2 g), and sulfuric acid (0.03 ml) under nitrogen. For each day of the reaction 0.03 g of diphenylamine (recrystallized) was added. The progress of the reaction was followed by tlc, and after 16 days quantitative conversion to product was detected. The solvent was removed under reduced pressure and methanol (20 ml) which was cooled to −78° was added, followed by enough ammonium hydroxide to make the solution slightly basic. The insoluble residue was extracted twice with boiling methanol (10 ml), the methanol solutions were combined, and then the solution was reduced to dryness under vacuum. After recrystallization from toluene,

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propanol, and toluene, 2.2 g (73%) of 6-methyl-1-vinyluracil was obtained as white needles: mp 198.5–200.5; ir 3500 (m), 3030 (s), 2850 (s), 2480 (w), 1780 (s), 1470 (m), 1440 (m), 1380 (s), 1326 (m), 1225 (m), 1192 (m), 1685 (w), 1040 (m), 975 (m), 940 (m), 870 (m), 840 (m), 722 (w), 755 (m), 712 cm^{-1} (m); nmr (DMSO-d_6) (relative to TMS) δ 2.50 (s, 3 H, 6-Me), protons 5.92 (s, 1 H, 5 proton), 5.80 (d, J = 8 Hz, 2 H, β-methylene proton); 6.80 (q, J = 16 Hz, J = 8 Hz, 1 H, α-vinyl proton). *Anal.* Calcd for $C_7H_8N_2O_2$: C, 55.25; H, 5.29; N, 18.41. Found: C, 55.60; H, 5.40; N, 18.32.

Polymerization Initiated by γ Radiation. Monomers either in solution or in the solid state were degassed in glass polymerization tubes under 0.1-mm vacuum at −78° for at least 20 min. The tubes were sealed under vacuum and were then irradiated under the conditions given in Table I. The polymers were isolated by precipitation and washing with methanol, followed by dissolution in 0.1 M sodium hydroxide, filtration through Millipore Teflon filters, and precipitation by acidification with 0.1 M hydrochloric acid. After the polymers were washed with distilled water several times they were dried at 150° (0.1 mm) overnight. *Anal.* Calcd for poly(1-vinyluracil), $(C_6H_6N_2O_2)_n$: C, 52.16; H, 4.37; N, 20.28. Found: C, 52.13; H, 4.85; N, 20.26 (experiment 3); C, 52.08; H, 4.52; N, 20.10 (experiment 5); C, 52.13; H, 5.14; N, 20.28 (experiment 9). Calcd for poly(6-methyl-1-vinyluracil), $(C_7H_8N_2O_2)_n$: C, 55.25; H, 5.29; N, 18.41. Found: C, 55.09; H, 5.42; N, 18.26 (experiment 11).

Acknowledgment. Acknowledgment is given to Drs. Plass, McIntyre, and Imada of the Physics Department for allowing us to use the cobalt-60 source.

Radiation Cross-Linking of Polydimethylsiloxane. Cross-Linking and Fracture by Solubility Analysis

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ABSTRACT: Estimates of G values for cross-linking (X) and fracture (F) have been made from experimental determinations of the gel fraction formed by Co-60 γ-irradiation of polydimethysiloxane. Estimates were made for an oil (M_w = 8.5 × 10^4) of G(X) = 2.2 ± 0.3 and G(F) = 0.7 ± 0.2. For a rubber (M_w = 4.8 × 10^6), G(X) ≃ 2.3. When samples were cooled with liquid nitrogen during irradiation the yield of cross-links was depressed to one-half to two-thirds the value observed on irradiation at room temperature. Inclusion of 10%, by weight, of diethyl disulfide in the oil greatly decreased the yield of cross-links: G(X) = 0.8, G(F) ≃ 0.4. This observation provides evidence that at least two-thirds of the cross-links are formed from free radical precursors.

As part of an extensive study of the radiation chemistry of polydimethylsiloxane, Miller included yields of cross-links estimated on the simplifying assumption that concurrent fracture of the polymer molecules was negligible.[2] Kilb has shown that the dependence of limiting viscosity number on radiation dose can be analyzed to provide an estimate of the ratio of fractures to cross-links. However, the method was rather insensitive and only allowed the conclusion that the ratio was less than one for a polydimethylsiloxane exposed to electrons. A more precise upper limit of one-half was deduced from measurements of radiation-induced changes in molecular weight determined by both light scattering and by osmometry,[3] but this is still too high to justify the assumption that fracture may be neglected. Subsequently, in the course of a study concentrated mainly on electron spin resonance spectroscopy, Ormerod and Charlesby[4] mentioned that ratios of fractures to cross-links of 0.17 and 0.25, respectively, had been deduced from a sol–gel analysis of data previously reported by Charlesby[5] and by Miller.[2] The sol–gel analysis had been formulated by Charlesby and Pinner.[6]

The objective of the present work is to examine the applicability of the Charlesby–Pinner analysis to polydimethylsiloxanes and to extend its use to samples irradiated at low temperature and to samples including additives. These objectives were chosen to extend observations on the influence of these experimental variables made by Miller.[7]

Experimental Section

A sample of a polydimethylsiloxane oil (Vicasil 30,000) was donated by the General Electric Co. This is similar to the sample studied previously by Miller of weight-average molecular weight M_w = 8.5 × 10^4 ± 10%. Measurements of solution viscosity were made and found to be consistent with a weight-average molecular weight within these limits. A sample of a polydimethylsiloxane rubber of M_w = 4.8 × 10^6 was donated by the General Electric Co.

Samples of benzene and dodecanethiol were of laboratory reagent grade. A purified sample of diethyl disulfide was obtained from Mr. L. A. Miller.

Samples were thoroughly degassed by pumping *in vacuo;* the oil was repeatedly frozen until no more bubbles were formed on thawing. It was stripped of volatiles by heating for 24 hr in a vacuum oven at 100°. Measurements of solution viscosity showed that the molecular weight of the polymer remained within the limits mentioned above following this treatment. Each polymer sample was sealed in a glass ampoule at a pressure of <10^{-4} mm.

The ampoules were exposed to Co-60 γ-rays at an ambient temperature of 35° and at a dose rate of 0.3–0.8 Mrad/hr. Ampoules irradiated in liquid nitrogen were taped to the inside sector of a Dewar flask which faced the Co-60 source. Immediately after

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