PVC, probably highly syndiotactic, that is not detected by proton nmr. The tacticity analysis in Table I based on ^{13}C data, at this time, should also be considered as an analysis of the portion of PVC soluble in *o*-dichlorobenzene. Future work may establish what effect crystalline PVC has on its ^{13}C nmr spectrum.

Acknowledgment. I gratefully acknowledge the contributions made through the many helpful discussions held with Professor S. Krimm, University of Michigan, on conformation in PVC.

Nuclear Magnetic Resonance Relaxation in a Radiation Cross-Linked Poly(vinyl chloride) System

D. D. Davis and W. P. Slichter*

Bell Laboratories, Murray Hill, New Jersey 07974. *Received July 6, 1973*

ABSTRACT: Nmr relaxation measurements were employed to investigate the effect of mixing and subsequent irradiation on the segmental mobility of a 2:1 mixture of poly(vinyl chloride) (PVC) and bifunctional tetraethylene glycol dimethacrylate (TEGDMA). Mixing decreases TEGDMA mobility while the glass transition of PVC is markedly depressed. As a PVC-TEGDMA mixture is initially heated above room temperature, there is a decrease in number of mobile molecular segments. The cause is attributed to development of paracrystalline order in the PVC. Irradiation produces strong motional hindrances, even impeding methyl group rotation. The effect becomes important at a dose of about 0.05 Mrad.

In recent studies[1,2] the chemistry and some physical properties of a commercially useful electron-irradiated poly(vinyl chloride)-tetraethylene glycol dimethacrylate (PVC-TEGDMA) cross-linked system were investigated. Added to increase the sensitivity of PVC to cross-linking, the bifunctional TEGDMA self-polymerizes in the early stage of cross-linking, but with increasing irradiation forms a network with PVC. The effects of composition and electron dosage upon gel formation were observed, and morphological, calorimetric, and dynamic mechanical findings were related to the chemistry of the cross-linking. In the present work, we have studied the segmental mobility of the PVC-TEGDMA network system at a molecular level as seen by nmr relaxation measurements.

Experimental Section

Materials. The PVC used was Opalon 660 (Monsanto) which is reported to have a weight-average molecular weight of 120,000 and a number average of 50,000. The tetraethylene glycol dimethacrylate, a liquid, is a product of the Ware Chemical Corp.

The PVC-TEGDMA mixtures were prepared by W. A. Salmon using a weight composition ratio of PVC to TEGDMA of 2:1. The substances were mixed with heat stabilizers in a blender at 80°, compression molded under 15-tons ram force at 140° for 3 min, and irradiated by 1-MeV electrons at a rate of 0.01 Mrad/sec to attain the desired radiation dosage.[1] Uniformity of composition and morphology is difficult to achieve within a batch or from batch to batch through this series of processes. Except for the 5-Mrad sample which was red, all samples were colorless. Sample thickness was about 0.04 in.

Procedure. The nmr measurements determined the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2, as functions of temperature and radiation dose.[3] The pulse method of nmr was used at a resonance frequence of 30 MHz in an apparatus previously described.[4] T_1 was determined using a conventional 180-90° pulse sequence, while T_2 was obtained by measurement of the free induction decay following a 90° pulse.

In all the samples of this study, it was found that at sufficiently high temperature the free induction decay could be decomposed by computer analysis into a weighted sum of two exponential decays.[5] These decay components were separated and the calculated T_2 relaxation times and their relative intensities which are referred to hereafter as the mobile and immobile fractions plotted *vs.* temperature.[6] The terms mobile and immobile are to be understood as relative to each other. Computer calculated uncertainty ranges for the decay curve fits were too small to warrant inclusion on the data plots. In the case of a two component relaxation, the longer T_2 is associated with the mobile protons while the shorter T_2 is associated with the relatively immobile protons. Coincidentally, for the PVC-TEGDMA composition used in this study the protons residing on the PVC and the TEGDMA molecules are nearly equal in number.

Sample temperature was maintained suitably constant by means of a Leeds and Northrup 6261 controller; 5 min was necessary for an observation while 20 min was allowed between observation for the purpose of sample temperature equilibration.

Results

We have sought to resolve the effect of the mixing and subsequent irradiation on the segmental mobility of these PVC-TEGDMA mixtures. To do so we have examined the nmr behavior of the individual components and of a series of mixtures exposed to irradiation doses varying from 0 to 5 Mrad.

T_2 Relaxation Time. The T_2 and mobile fraction variations with temperature for PVC, TEGDMA monomer, and its polymer are given in Figure 1. The poly(TEGDMA) was produced by heating the monomer at 120° overnight to polymerize thermally into a three-dimensional network.

The mobile fraction *vs.* temperature dependence of PVC resembles the pattern of the stiffness modulus-temperature data published by Reding *et al.*[7] for a PVC polymerized at 40°. In that study the stiffness modulus dropped steeply at the glass transition, but then decreased gradually with increasing temperature. The existence of this "plateau" region was attributed to paracrystallinity (two-dimensional chain alignment). The PVC used in this work begins to display molecular motion on the T_2 scale at 120°. The initial steep rise in mobile fraction presumably is caused by the amorphous portions. The gradual ascent between 130 and 200° may be due in

---

(1) W. A. Salmon and L. D. Loan, *J. Appl. Polym. Sci.*, **16**, 671 (1972).

(2) H. E. Bair, M. Matsuo, W. A. Salmon, and T. K. Kwei, *Macromolecules*, **5**, 114 (1972).

(3) A concise review of NMR relaxation times is given by D. W. McCall, *Accounts Chem. Res.*, **4**, 223 (1971).

(4) W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **35**, 10 (1964).

(5) D. W. McCall and D. C. Douglass, *Polymer*, **4**, 433 (1963).

(6) S. Kaufman and D. J. Bunger, *J. Magn. Resonance*, **3**, 218 (1970).

(7) F. P. Reding, E. R. Walter, and F. J. Welch, *J. Polym. Sci.*, **56**, 225 (1962).

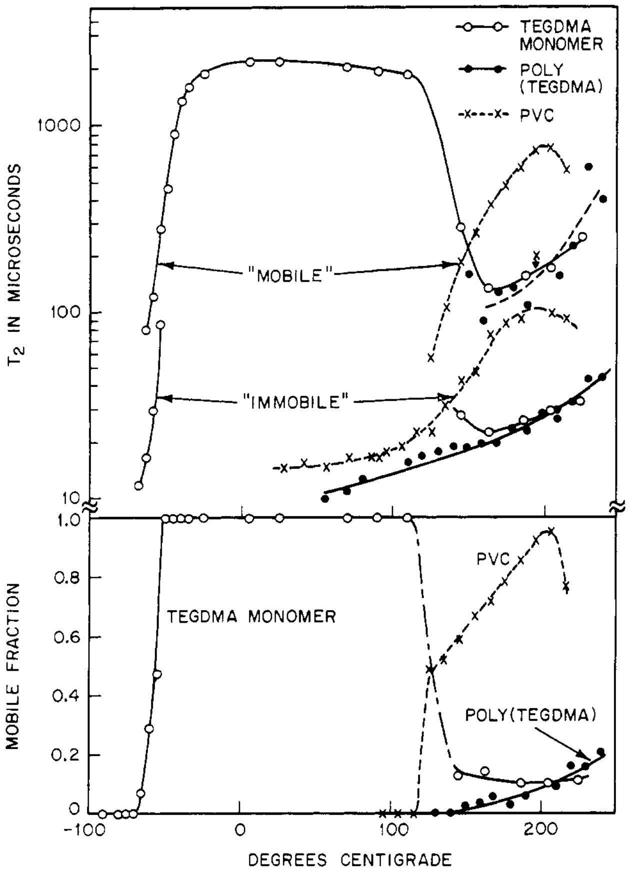

Figure 1. T_2 and mobile fraction *vs.* temperature for PVC, TEGDMA, and poly(TEGDMA).

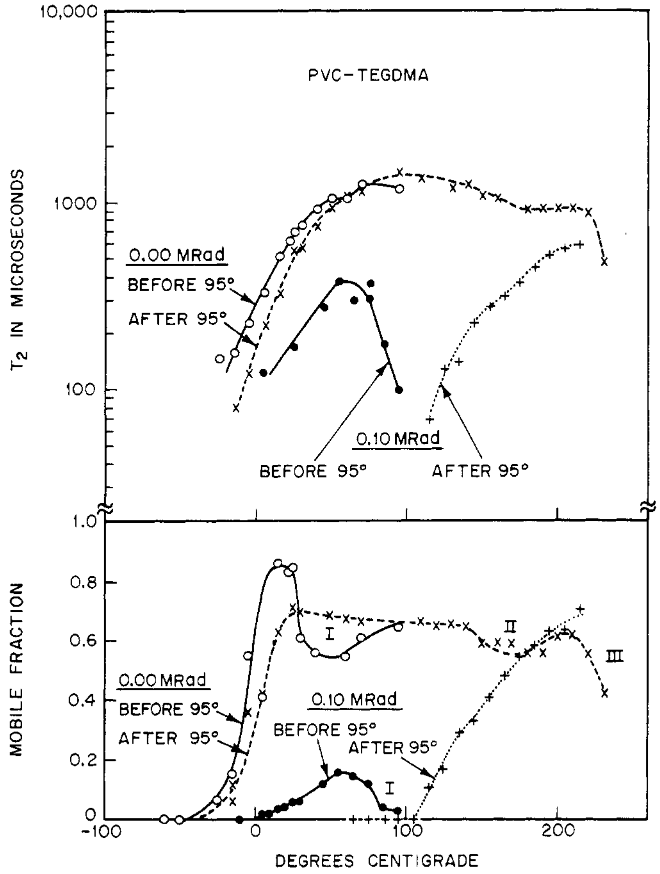

Figure 2. Long T_2 and mobile fraction *vs.* temperature for 0.00- and 0.10-Mrad PVC-TEGDMA mixtures showing the effect of a 95° heat treatment. Short T_2 is omitted for clarity.

part to the melting of paracrystalline regions. The downtrends in both parameters above 200°, seen repeatedly in the PVC-containing materials of this study, is attributed to thermally activated cross-linking. Chain stiffening due to creation of olefinic bonds by way of PVC dehydrochlorination may contribute to the downtrend.

As seen in Figure 1, TEGDMA monomer becomes liquid like about −50° and at 115° thermally polymerizes extensively. The near constant T_2 at about 2 sec is the result of the magnetic field inhomogeneity limitation. By 160° the conversion into network polymer no longer progresses and the newly formed material exhibits the same T_2 behavior as does the poly(TEGDMA) sample. Mobility increases beyond this temperature are modest in terms of both amplitude and number of participating groups.

The result of mixing the monomer and PVC together is shown in Figure 2 where the long T_2 and mobile fraction are presented for an unirradiated PVC-TEGDMA mixture (0.00 MRad) and a mixture irradiated to 0.10 MRad. Note the occurrence of minima in the mobile fraction with related effects in the T_2 behavior. These indicate the existence of motion-hindering changes in the material. There are three such minima for the 0.00-MRad sample. Each minimum is assigned a Roman numeral for identification, the minimum at lowest temperature being designated I. Minimum III, although not complete for this sample since the experiment was not pursued to high enough temperature, has been observed as a complete minimum in the experiment on the 5-MRad sample. Aside from some inexplicable scatter, for samples having the same irradiation treatment the data are not closely reproducible. The apparent cause is lack of material uniformity. We accept the observed magnitudes as being usefully representative.

In the case of minimum I, after heating sufficiently above the center of the minimum (95° was used), cooling and then reheating, the T_2 transition and mobility onset were relocated several degrees higher. Likewise, the minimum had disappeared.

For the mixture moderately irradiated to 0.10 MRad the effect manifested by similar heating is drastic. A 95° temperature was again chosen because it was sufficiently high to be in the region of decreasing mobility, and also would conform to the previous case. As shown in Figure 2, the initial mobility is lost and the onset of the T_2 transition occurs about 110° higher. It would be convenient to adapt the term "heat treat" to this process.

A composite graph comprising the T_2 and mobile fraction data for several samples (0.00, 0.06, and 5 MRad) is furnished in Figure 3 to show the effect of increasing irradiation dose upon the mixture. In general, the first two minima become less conspicuous as cross-linking density increases.

The data for another 0.00-MRad sample from the same preparation batch as the one in Figure 2 is given in Figure 3 to illustrate the discrepancies encountered as a result of sample nonuniformity. A third unirradiated sample was measured which was from a different batch. Since the data from all three of these are averaged for later calculation, the mobile fraction magnitudes for this third sample are reported here as 0.78 at 20°, 0.72 at 50°, and 0.87 at 100°.

Nmr T_2 transitions, though directly related to the dilatometric glass transition, occur typically 50° higher because of the shorter correlation time. Selecting a temperature to represent the glass transition in these broad T_2 transition materials is a somewhat arbitrary procedure, especially when they have been strongly irradiated. But

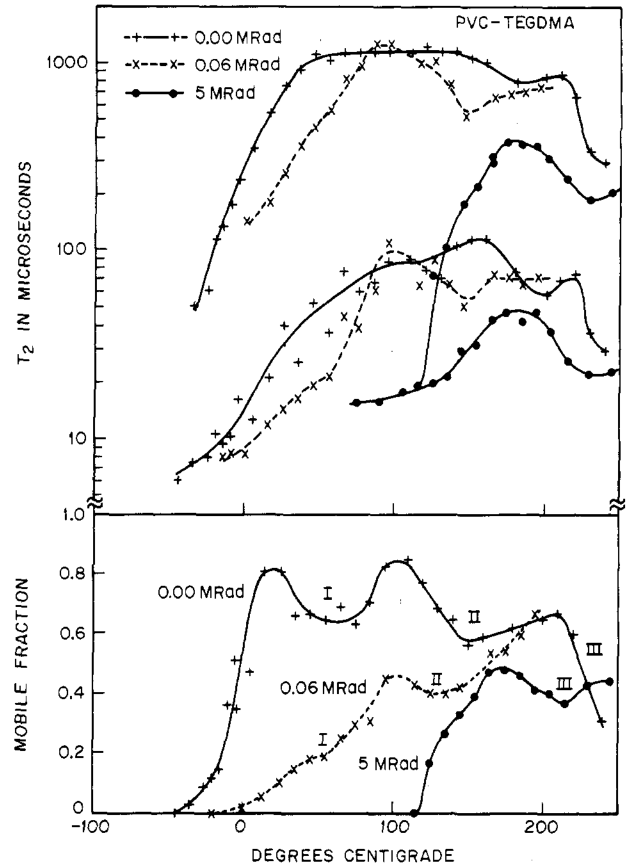

Figure 3. T_2 and mobile fraction *vs.* temperature for 0.00-, 0.06-, and 5-Mrad PVC-TEGDMA mixtures.

the appearance of a second component having longer T_2 in the free induction decay as temperature is raised is an obvious indication of the onset of mobility. Therefore, the temperature of this appearance has been taken as the glass transition. These temperatures are given in Table I to show the effect of cross-linking. Up to 0.10-MRad dose this dependence is approximately linear. There may be as much as a five degree upward shift at the gel point. Linearity does not extend, however, to high irradiation dosage, since as the cross-links occur they stiffen the matrix making further reaction less efficient due to decreased mobility.[8] Also shown in the table are the new temperatures of mobility onset after the unirradiated and the 0.10-MRad mixtures were heated to 95°, cooled, and reheated.

In the temperature range 200-240°, all the PVC-TEGDMA materials become comparable in magnitudes of mobile fraction and T_2. The more densely cross-linked materials show such correspondence in the higher portion of this range.

T_1 **Relaxation Time.** The T_1 dependence on temperature for both the TEGDMA monomer and polymer is shown in Figure 4. Since T_1 in liquids is often controlled by dissolved oxygen, the monomer sample was thoroughly degassed. The minima at −170 and 30° for the monomer are ascribed respectively to methyl rotation and general mobility. Above room temperature the T_1 dependence becomes less steep with increasing temperature which may indicate a small amount of monomer polymerization. At 115° extensive thermal polymerization of monomer results in a steep drop in T_1 as network polymer is formed. The T_1 of the newly polymerized monomer then conforms with that of the polymer as was seen also in the T_2 observations.

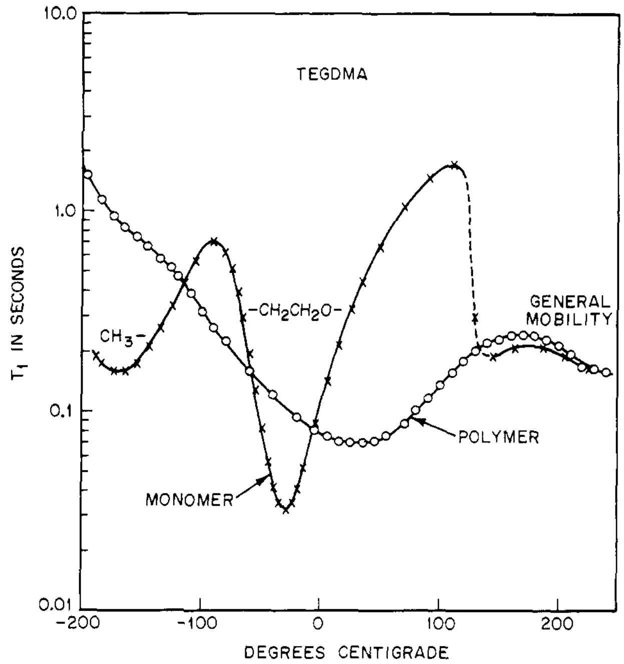

Figure 4. T_1 *vs.* temperature for TEGDMA monomer and polymer.

Table I

Sample Irrad Dose (Mrad)	Mobility Onset Temperature (°C) Initial	Mobility Onset Temperature (°C) After 95° Heating
0.00	−43	−39
0.04	−30	
0.05	−25	
0.06	−15	
0.08	−10	
0.10	−2	+105
5.0	+120	

Poly(TEGDMA) suffers severe motional constraints. Although the T_1 minimum ascribed to methyl rotation is prominent at −170° in the monomer, it appears only as a bend in the curve for the polymer at this same temperature. If both these effects relate to methyl rotation, the energy barrier to the motion is about the same in the monomer and the polymer, since the relaxation is at the same temperature in each. But the relaxation is less effective than in the monomer as indicated by the higher magnitude of T_1, apparently due to fewer groups participating. The minimum at 25°, arising from the restricted mobility of the ethylene glycol groups located between the network anchor points is very broad, suggesting a broad distribution of correlation times. Large-scale motions of the network polymer are retarded until about 250°.

The effects of cross-linking induced by electron irradiation on the T_1 of a PVC-TEGDMA mixture are shown in Figure 5 where the data for an unirradiated material (0.00 MRad), moderately (0.06 MRad), and strongly (5 MRad) irradiated materials, as well as a pure PVC, are presented. Three minima are seen in the temperature range observed. The low-, middle-, and high-temperature minima are attributed respectively to the motions of the methyl, tetraethylene glycol, and vinyl chloride groups. Above 60°, there were often two T_1 signals evident in the mixtures, their presence being most obvious in the least irradiated materials. The signals sometimes overlapped precluding

---

(8) A. Charlesby, *Advan. Chem. Ser.*, 66, 5 (1967).

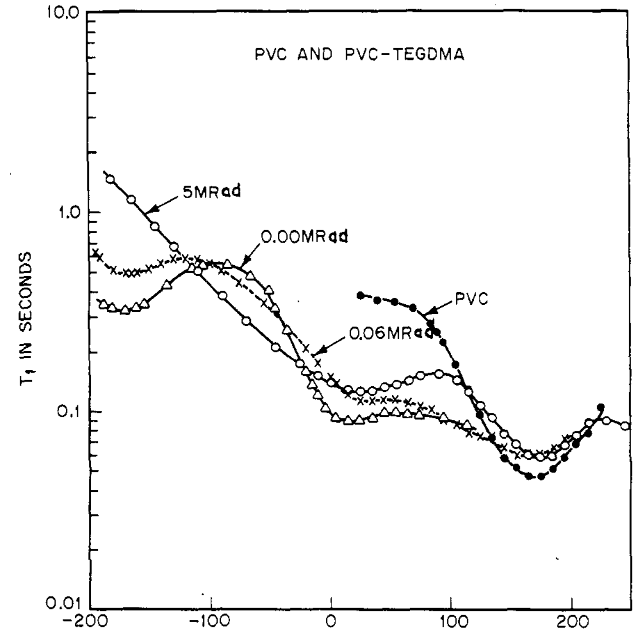

Figure 5. T_1 *vs.* temperature for 0.00-, 0.06-, and 5-Mrad PVC-TEGDMA mixtures and PVC.

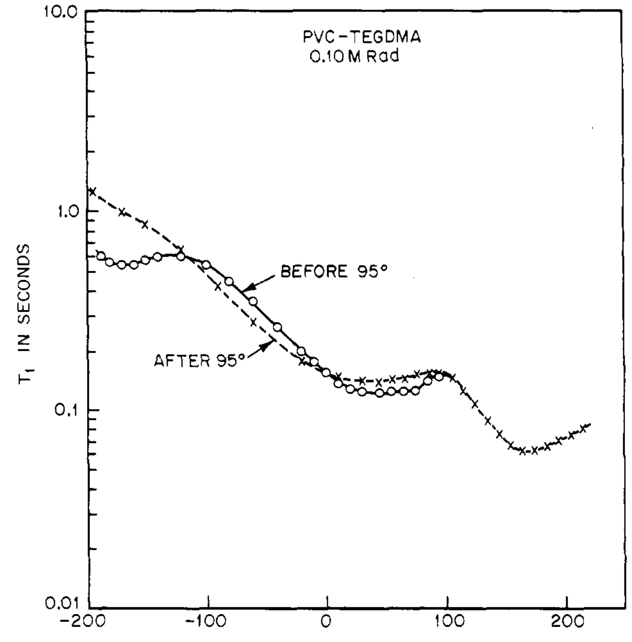

Figure 6. T_1 *vs.* temperature for 0.10-Mrad PVC-TEGDMA mixture showing the effect of a 95° heat treatment.

resolution. This is why the vinyl chloride group minimum for the 0.00-MRad mixture is not shown on the graph.

As a result of the mixing, the ethylene glycol T_1 minimum of the TEGDMA is shifted upward by about 50°. The high-frequency motions of the PVC chains occur 150° higher yet which is the same as in the homopolymer. As the material is irradiated to 0.06-MRad dose, even the methyl rotation is impeded, for its minimum appears 5° higher.

The effect of heat treating the 0.10-MRad PVC-TEGDMA mixture at 95° is shown in Figure 6. The solid curve depicts the behavior prior to exposure to the 95° temperature, and the dashed curve shows the result. A similar treatment was performed on an unirradiated material, and the minimum in T_1 which had occurred at 18° with T_1 equal to 100 msec was found to have been altered to 25° with T_1 equal to 110 msec. These data reveal that the ethylene glycol and methyl groups of the TEGDMA have been subject to a new motional restriction as a result of the 95° heating. The relatively small amount of TEGDMA thermal cross-linking at this temperature must be responsible.

Table II summarizes the data.

Discussion

Unirradiated Mixture. Conventional poly(vinyl chloride) is an essentially amorphous material which possesses sufficient paracrystallinity to be detectable by X-ray diffraction.[9] In the work of Reding,[7] mentioned earlier, it was found that changing the polymerization temperature substantially alters the stiffness modulus transition of PVC. This was explained by increases in the amount of order brought on by greater production of syndiotactic structure at lower temperatures.

The nmr data fail to show a first-order transition for the TEGDMA monomer. The latter result confirms Bair's work.[2] Additionally, the substantial temperature difference between the T_2 transition (Figure 1) and the ethylene glycol T_1 minimum (Figure 4) also suggest that TEGDMA is glassy at low temperatures. Hence, if a PVC-TEGDMA mixture survives the mixing and molding processes prior to irradiation without undergoing thermally activated crosslinking, the resulting material should be a highly plasticized amorphous substance with some low-degree order possible within the PVC chains.

The mobility which occurs in the unirradiated mixture at the lower temperatures is predominately because of the TEGDMA. Assuming that up to 100° all the TEGDMA protons are motionally free, then taking the average of the mobile fraction data for the three unirradiated samples, the fraction of all PVC protons which are mobile is estimated as 0.6 at the mobile fraction peak just prior to minimum I (20°), 0.3 at minimum I (50°), and 0.6 after completion of the minimum (100°). Thus, about 0.3 of the PVC protons lost mobility as temperature increased. This is equivalent to 0.15 of all protons and 0.20 by weight of the total material (*i.e.*, 0.15 × 1.33).

In their work on the PVC-TEGDMA mixtures, Bair *et al.*[2] proposed that the transitions they observed were related to PVC-rich and TEGDMA-rich phases of 100-Å size. These are dispersed in and between larger PVC domains of 1-μ size which result from the inability of the mixing process to produce uniform mixing on a minute scale. A desorption experiment by Bair demonstrated that the amount of pure TEGDMA phase separation upon cooling TEGDMA saturated PVC from 80° to room temperature was insignificant. Before irradiation the PVC-rich phase is the more rigid, and as the cross-linking density increases there is a growth in quantity of rigid phase.

The mobile and immobile fractions mentioned in this work do not necessarily correspond to the two morphological phases cited by Bair and coworkers, for the protons of both PVC and poly(TEGDMA) are to be found in each fraction, as observed in the homopolymers. Protons near entanglements in the larger PVC chains and those near cross-link points in both kinds of molecule can be expected to be in the immobile category. The PVC "crystallites" will also restrict molecular motion. Up to 100° the dominant contribution to the mobile fraction of the unirradiated mixture originates in the TEGDMA-rich phase. Immo-

---

[9] A. J. Brunner, *J. Polym. Sci., Part B*, 10, 379 (1972).

Table II

Sample Irrad Dose (Mrad)	T_1 Minima					
	Low		Middle		High	
	Temp (°C)	T_1 (msec)	Temp (°C)	T_1 (msec)	Temp (°C)	T_1 (msec)
0.00	−170	317	20	91	175[a]	69[a]
0.04	−172	345	20	98	(No data)	
0.05	−172	445	20	107	?[b]	?[b]
0.06	−165	490	~25	115	170	61
0.08	−162	545	~35	119	170	60
0.10	−165	520	~45	124	170	62
5			25	128	175	59

[a] Observed in a sample from a new batch of material. [b] Minimum is obscured because of presence of two T_1's.

bile material resides in either phase and comprises the remaining rigid PVC segments and the few thermally cross-linked network poly(TEGDMA) molecules existing at this temperature.

The source of minimum I is uncertain. The following conjecture is proposed as an explanation. Disorder was introduced in the PVC by mastication during mixing. The molding process was applied too quickly to allow molecular relaxation to alleviate the disorder. As the temperature was raised during the nmr experiment, some of the disorder was eliminated as PVC chains were enabled to remove chain conformation distortions, and, perhaps, even acquire lateral alignment.

We postulate that as temperature rises the following occurs in sequence in the unirradiated mixture: (1) all the TEGDMA becomes mobile, (2) more than half the PVC becomes mobile, (3) almost half the already mobile PVC begins to lose mobility as these chains become more ordered causing minimum I, (4) above 50° TEGDMA thermally polymerizes to a small but increasing degree and, finally, (5) the former mobility of the material is regained if not surpassed by 100°. PVC protons remaining immobile at 100° are likely residing on molecules involved in the paracrystalline ordering. These eventually become mobile with increasing temperature but the change is obscured by subsequent events.

In their calorimetric study of the ungelled samples, Bair and coworkers observed a transition around 40° which was higher in temperature than the PVC phase and TEGDMA phase transitions by about 70 and 100°, respectively. This transition, designated IIIB, appeared to merge with the PVC phase transition as the gel point was reached, but was not seen in the viscoelastic experiments. Speculation was offered that IIIB might be due to a small amount of a more rigid phase.

It is plausible that our minimum I has the same origin as the unexplained IIIB transition. Generally, minimum I also became less conspicuous in the region of gelling dose (the exception being the 0.10-MRad sample). The specific heat transition temperatures were given as −64, −33, and 40° for the TEGDMA phase, PVC phase, and IIIB transitions. If we were to interpret our data in the same manner, that is, distinct phase transitions, we might estimate the mobile fraction transition temperatures in the unirradiated mixture (Figures 2 and 3) as being −40° for TEGDMA (temperature of initial mobility) and −5° for PVC (temperature at which mobile fraction exceeds 0.5) while minimum I would be about 50°. The differences in observed temperatures between the two experiments for these supposedly similar mechanisms appear to correspond roughly.

Using Bair's C_p data for the unirradiated mixture, we calculate that transition IIIB constitutes 13% of the total change up to that temperature. Since our nmr study reveals that only approximately 0.8 of the material has experienced motion to this point, we deduce that the transition represents about 10% of the total material. This is to be compared with our estimate of about 20 wt % of matter losing mobility during minimum I in the unirradiated mixture and 17 wt % in the 0.10-MRad mixture (to be mentioned).

Minimum II, occurring around 150°, is undoubtedly the result of extensive thermally activated TEGDMA polymerization. Presumably, the process is slowed by stiffening and dilution effects introduced by the presence of PVC as the major component. As the PVC chains adjacent to clusters of network poly(TEGDMA) must also experience new motional constraints, it is surprising that the T_2's decrease so little.

By 200° we expect poly(TEGDMA) in the mixture to be more mobile than in the pure polymeric state because its network will be less dense. Using the mobile fractions of Figures 1 and 2 for these materials, we can estimate that nearly all the PVC protons and about three-tenths of the poly(TEGDMA) protons are mobile. Thus, the proportion of mobile poly(TEGDMA) protons in the mixture is about four times larger than in the pure polymer at this temperature. Furthermore, as shown by the T_2 magnitudes, a mobile poly(TEGDMA) proton in the mixture is more mobile than one in the pure polymer.

Above 200° the PVC begins to degrade substantially as thermally activated radical formation leads to competition between chain scission and cross-linking. Degradation rates for PVC depend on time, temperature, and the nature of ambient atmosphere. There appears to have been belief that, in air, radical formation in PVC induces chain scission in preference to cross-linking.[10] Minimum III indicates that cross-linking is the dominant route pursued in these mixtures as both mobile fraction and T_2 exhibit strong downtrends indicating the onset of new rigidizing influences. Support for this view can be found in several other studies.[11-13]

Although the experiment on the unirradiated sample was not pursued to sufficiently high temperature to observe the rise in mobility which follows the downtrend due to PVC cross-linking, the rise was plainly evident in the 5-MRad sample experiment. This rise may signify that chain scission has become the dominant mechanism of thermal degradation at this temperature.

In a mixture similar to the type studied herein, composed of PVC, poly(methyl methacrylate), and some PVC–MMA graft copolymer, it was learned[14] that in a nitrogen atmosphere chlorine radicals released from PVC attacked the PMMA inducing chain scission. At 210° the PMMA degraded faster than if pure while the PVC degraded more slowly than if pure. If the same pattern were to be followed in air, then the mobility rise which is observed in this work at temperatures above the range of the PVC cross-linking may be due appreciably to poly(TEGDMA) degradation as well as PVC degradation.

Effect of Irradiation Cross-Linking. The gel point for the series of irradiated PVC–TEGDMA mixtures occurred between the doses 0.05 and 0.06 MRad in agreement with

---

(10) W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).

(11) D. Druesedow and C. F. Gibbs, *Mod. Plast.*, 30, 123 (1953).

(12) N. K. Baramboin, "Mechanochemistry of Polymers," Maclaren & Sons, Ltd., London, 1964, p 126.

(13) C. H. Fuchsman, *Advan. Chem. Ser.*, **85**, 18 (1968).

(14) A. Guyot, M. Bert, A. Michel, and R. Spitz, *J. Polym. Sci., Part A-1*, 8, 1596 (1970).

the experiments of Salmon and Loan.[1] This was evidenced by the broadening of temperature range of the mobile fraction transition especially and also of the T_2 transition (Figure 3). This broadening is a typical manifestation of the gel point. At the gel point interpolymer is being formed. The gel, it is seen, hinders molecular motion on even the short-range nmr scale as well as decreasing the number of atoms participating in the motions.

Generally, by increasing the irradiation beyond the gel point dose, the peak in mobile fraction occurring just prior to minimum I becomes less prominent since PVC chains are being cross-linked and there will be less reordering with temperature rise. In the 0.10-MRad sample the peak is anomalously more prominent than would be expected for this dosage. In this sample the bulk of the material is so highly cross-linked (92% TEGDMA, 20% PVC[1]) that its T_g is far higher than and quite distinct from that of the most mobile material. Referring to Figure 2 this difference is shown by the mobile fraction peak occurring at 60° which is well separated from the bulk material's transition. Though the major part of this minimum I process is attributed to PVC reordering as in the unirradiated mixture, TEGDMA cross-linking may possibly contribute to the downtrend because of the higher temperature involved here. Assuming that the 0.03 mobile fraction remaining at 95° during the initial heating is all TEGDMA, and subtracting this amount from the maximum mobile fraction, 0.16, at 60°, one estimates that 0.13 of the protons are involved in the mobility loss. Considering these to be PVC protons, they constitute 0.17 by weight of the total material (*i.e.*, 0.13 × 1.33). This is the figure used for the 0.10-MRad sample in the transition IIIB comparison.

When a cross-linked material is a homopolymer, T_g will increase linearly with the number of cross-links.[15,16] The interpolymer being formed beyond the gel point of the present mixture is a graft copolymer in which there exists a competing drive to lower T_g due to the presence of copolymer.[16] Therefore, linearity in the dependence of the mobility temperature on irradiation dose may not occur. Up to 0.10 MRad the temperature of the onset of mobility is about linearly related to dose. Salmon found from studies of physical properties[1] and of the swelling ratio[17] that irradiation has a marked effect on these materials up to this dosage. Although cross-linking continues to develop with higher levels of irradiation, it has relatively little effect on these properties. Similarly in the present studies, the mobility changes rapidly with increasing dosage up to about 0.10 MRad. At higher levels of irradiation, however, further changes in mobility occur only gradually. Following exposure to heavy irradiation as in the 5-MRad sample, most of the PVC is cross-linked (81%[1]) and the minimum I process vanishes. If the slight shoulder at 155° in both mobile fraction and T_2 is real, it could be a vestige of minimum I. Completion of reaction of the 2% residual unsaturation in this material[1] cannot account for the shoulders.

Despite the large amount of interpolymer in the 5-MRad material, the mobile fraction and T_2 transitions fortuitously commence at the same temperature as in PVC itself. This early mobility should be due to lightly cross-linked poly(TEGDMA) and the small amount of uncross-linked PVC remaining. The latter would be the smaller size chains of this polydisperse PVC since small chains are reportedly[18] more difficult to radiation cross-link.

Also, in this material the high-frequency motions of the PVC molecules, as disclosed by T_1 behavior, do not appear to be significantly restricted. The degree of cross-linking in the material is the controlling factor and will be computed now for the 5-MRad material. The critical cross-linking index[19] at the gel is

$$\gamma_{\text{gel}} = \frac{\overline{M}_{\text{n}}}{\overline{M}_{\text{w}}} = \frac{5 \times 10^4}{12 \times 10^4} = 0.42 \text{ cross-linked unit}/\overline{M}_{\text{n}} \text{ chain}$$

This corresponds to one cross-linked unit per 1900 vinyl chloride repeat units. Salmon and Loan[1] calculate that $G_{\text{cross-links}}$ in gelled material has fallen to 1/25th of its value near the gel point (0.05 MRad). For the 5-MRad material, therefore, the cross-linking degree is

$$\frac{1}{25} \times \frac{5 \text{ MRad}}{0.05 \text{ MRad}} \times \frac{1}{1900} = 1 \text{ cross-linked unit}/475 \text{ repeat units}$$

There being 800 repeat units/number-average molecule, this result stipulates an average of about two cross-linked units per molecule. This then is inadequate to hinder high-frequency segmental motions. Overall mobility, though, on the T_2 scale has been reduced substantially since the T_2 and mobile fraction of the 5-MRad material above 150° are but one-half those of PVC homopolymer. As a reviewer has suggested, it may be that this effect results from a limitation on the isotropic reorientation of the chain motions owing to the cross-linking.

Thermally activated cross-linking of PVC occurs about 20° lower in the 5 MRad material than in the unirradiated form. There is a justification for this. Prior irradiation of PVC has been found[20] to increase the rate of subsequent thermally activated dehydrochlorination by the creation of labile sites. Dehydrochlorination is a step in PVC thermal cross-linking.[11] Hence, the presence of these preformed radical sites may be responsible for a larger amount of cross-linking at a given temperature in this range than in unirradiated material.

Summary

Heating a PVC–TEGDMA mixture beyond room temperature allows reestablishment within the PVC of order which had been lost during mixing. The process involves about 30% of the PVC. At higher temperature TEGDMA monomer homopolymerizes and at yet higher temperature PVC cross-links. Radiation cross-linking beyond 0.05-MRad dose results in strong motional hindrances and the tendency of PVC to reorder declines. High-frequency motions of the PVC, though, are not substantially affected even at quite high radiation dose. On the other hand, within the poly(TEGDMA) the number of methyl groups rotating at high frequency is appreciably decreased by moderate radiation cross-linking of these molecules.

Acknowledgments. We are grateful to W. A. Salmon for providing the samples used in these studies. We also appreciate the helpful comments of H. E. Bair, D. W. McCall, and W. A. Salmon on the manuscript.

---

(15) P. Mason, *J. Chem. Phys.*, 35, 1523 (1961).

(16) S. Loshaek, *J. Polym. Sci.*, 15, 391 (1955).

(17) W. A. Salmon, private communication.

(18) A. Charlesby, *Plastics*, 18, 142 (1953).

(19) F. A. Bovey, "Effects of Ionizing Radiation on Natural and Synthetic High Polymers," Interscience, New York, N. Y., 1958, p 79.

(20) R. Salovey and H. E. Bair, *J. Appl. Polym. Sci.*, 14, 713 (1970).