Cross-Linking Poly(ethylene oxide) and Poly[oxymethylene-oligo(oxyethylene)] with Ultraviolet Radiation

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SYNOPSIS

Poly(ethylene oxide) (PEO) and poly[oxymethylene-oligo(oxyethylene)] (PEM) disks are cross-linked by exposure to 254 nm radiation. The rate of formation of cross-links is greatly enhanced by the presence of benzophenone, and an average cross-link density of up to 6 mol % of ethoxy units can be obtained after several hours of irradiation. The highly cross-linked polymers are insoluble in water or organic solvents and show improved physical properties for handling and the formation of free-standing films. Scanning calorimetry and polymer swelling are employed to characterize the polymers, and impedance measurements are reported for sodium salt complexes prepared from the cross-linked polymers. Dynamic modulus measurements show that, upon irradiation, PEO and PEM become cross-linked, elastomeric solids. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Salt complexes of oligo- and polyethers, including poly(ethylene oxide) (PEO), poly[oxymethylene-oligo(oxyethylene)] (PEM), and poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP), have been studied for use as solid polymer electrolytes in high-energy-density batteries and electrochromic devices.[1] A general observation is that the highest ionic conductivities are found in completely amorphous materials that are soft and sticky and do not readily form free-standing films. A variety of chemical methods[2-4] and gamma radiation[5] have been utilized to form cross-links to improve the mechanical and surface properties of these electrolytes. Other studies of cross-linking in oligo- and polyethers by similar methods have been directed toward applications such as surgical dressings,[6,7] controlled drug delivery,[6,8] and semipermeable membranes.[9]

Recently, Allcock and co-workers[10] reported that MEEP undergoes cross-linking by irradiation with UV light, with or without benzophenone added as a photoinitiator. PEO was also indicated to undergo a similar reaction, although these products were not characterized in the study. The ease, relative safety, and low cost of UV radiation in cross-linking PEO and PEM would provide significant advantages over other methods. The purpose of this research effort was to examine the effect of ultraviolet radiation on the ionic transport properties, rheology, and other physical properties of PEO and PEM.

EXPERIMENTAL

Sample Preparation

PEO (M_w = 5 × 10^6; Aldrich) was dissolved in CH_3CN, and the viscous solution cast onto Teflon and dried in air. The polymer was cut into disks (approximately 0.4 mm thick) and dried at 60°C *in vacuo* for 12 h. PEM (M_w 7.5 × 10^4) was prepared by a literature method,[11] and disks were formed in glass rings and dried as above. Samples containing

benzophenone (Spectrum, reagent grade) as a photoinitiator were similarly prepared; sublimation of benzophenone from the samples did not prove significant under these conditions. PEO solutions with benzophenone were handled under red light to avoid polymer scission, and disks were stored in the dark. PEM samples containing benzophenone were not noticeably degraded under ambient light. Following irradiation, benzophenone and low molecular weight byproducts were removed in an acetone wash.

Disks were sealed in 1 in. diameter quartz tubes and placed into a Rayonet rotating UV reactor fitted with Hg vapor tubes (254 nm). Irradiation time was varied from 5 min to 60 h. Samples were flipped midway through the irradiation to promote even exposure. Irradiated disks placed in deionized water swell isotropically relative to the extent of cross-linkage. The Flory–Rehner relation was employed to derive the cross-link density[12]:

$$n = -[\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2]/V_1[\nu_2^{1/3} - \nu_2/2]$$

where n is the cross-link density (mol/mL); ν_2, the unswollen polymer volume/swollen polymer volume; V_1, the molar volume of the solvent (mL/mol); and χ, the polymer–solvent interaction parameter. The interaction parameter, χ, for linear PEO with water of 0.45,[13] has been seen to provide reasonable results with cross-linked PEO samples[14] and was therefore employed in these calculations. Cross-link densities are reported in moles/liter and mole percent. Mole percent refers to the percentage of ethoxy units cross-linked in the polymer sample.

Salt complexes of $PEM_{50}NaClO_4$ and $PEO_{15}NaClO_4$ were formed by swelling cross-linked polymers with $NaClO_4$ (EM, reagent grade) in freshly distilled CH_3CN.[†] The swollen mass was gently stirred for 12 h, the solvent removed under vacuum, and the complexes dried at 60°C *in vacuo* for 12 h. X-ray diffraction of the products showed no peaks corresponding to salt crystals, and the polymer/salt ratios were confirmed for several samples by means of sodium atomic emission analysis.

Sample Characterization

Variable-temperature impedance measurements were performed using a computer-controlled Solartron 1260 impedance analyzer and a Sun ECO1 environmental chamber. Samples were prepared as pressed disks, placed between two stainless-steel electrodes in an air-tight Kel-F cell, and annealed at 70°C.

DSC measurements were obtained at a heating rate of 10 K/min using a DuPont DSC 2910. Samples were loaded in an inert atmosphere into hermetically sealed pans. All samples were quenched from above the melting point prior to measurement. Thermal transitions were recorded at the onset points. ^{1}H- and ^{13}C-NMR spectra of native and cross-linked polymers were obtained using a Bruker 300 MHz instrument; IR spectra of polymer films were obtained on a Nicolet 510P FTIR.

The dynamic modulus was measured in oscillatory shear between parallel plates in a Rheometrics (Piscataway, NJ) Model RDS-2 rheometer. Disks were cut from the cast and irradiated films, then pressed to the diameter of the plates (12.7 or 9.525 mm). Samples were held in the plates with a light (100–1000 g) compressive force to ensure good contact and to prevent slipping of the sample on the plates. Care was taken to make measurements at strain amplitudes of 0.03 or less, since the modulus sometimes appeared to decrease at higher strains. The sample temperature was controlled using a convection oven that closed around the sample and the plates. Nitrogen was used in the oven to prevent oxidation.

RESULTS AND DISCUSSION

UV-Vis spectra for PEO and PEM (Fig. 1) exhibit a strong absorption centered at 190 nm, corresponding to an $n-\sigma^*$ transition. The absorptivity in the frequency range produced by standard UV sources (250–300 nm) is, however, relatively low. The dispersion of a small quantity of a conjugated molecule such as benzophenone greatly increases absorptivity in this range and results in an increase in the rate and extent of the photochemical reactions observed. The benzophenone does not react chemically with the polymer.

Sample disks approximately 0.4 mm thick were irradiated; this thickness was dictated by the requirements for rheology measurements. Disks of this thickness containing benzophenone almost completely absorb or scatter radiation at 254 nm[‡] (Fig.

[†] Sodium salt complexes were chosen for study of ionic transport as base-line studies on the uncross-linked complexes are available (see Ref. 11b). In addition, these complexes are more readily dried than are those containing lithium salts.

[‡] The scattering of light in the semicrystalline PEO disks precludes accurate measurement of absorption in these samples. PEM, which is amorphous at ambient temperature, provides more useful data.
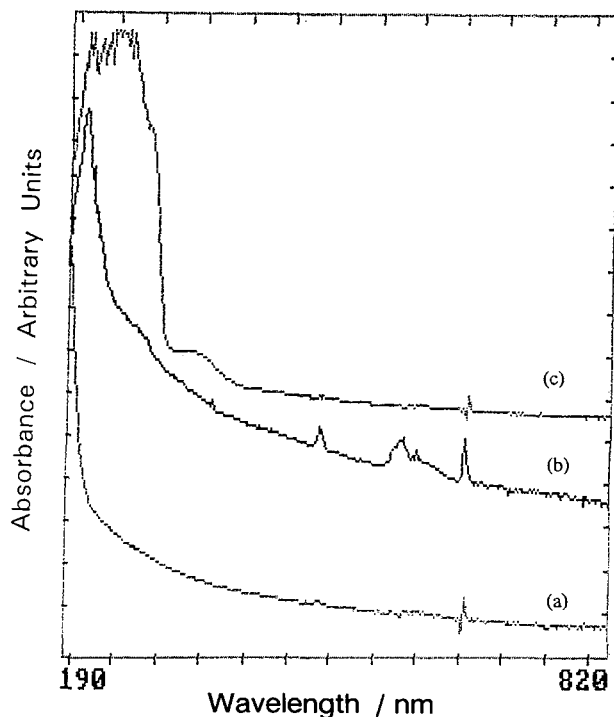
Figure 1 UV-Vis spectra for (a) PEO, (b) PEM, and (c) 0.5 mol % benzophenone in PEM.

2), and, therefore, the photochemistry does not occur homogeneously through the disk. As a compromise between reaction rate and product homogeneity, 0.5 mol % benzophenone was chosen. Although cross-link densities do not correlate well with transmittance data (because of the significant scattering of light), swelling tests indicate that cross-link density is greatest near the disk surface and

significantly less at the disk center; therefore, the cross-link density reported should be taken as a sample average and is subsequently referred to as the mean cross-link density.

Mean cross-link densities typically increased with irradiation time and are enhanced by 1 or 2 orders of magnitude by the addition of the photoinitiator. As can be seen in comparing samples 7–9 with 10–13 (Table I), a variation in the mean cross-link densities obtained is observed under similar controlled conditions. At very long irradiation times, the decrease in mean cross-link density may correspond to significant scission of the polymer chains.

The thermal transitions of irradiated samples are essentially unchanged from those of the native polymers. Glass transition temperatures for all PEO and PEM samples were between −60 and −62°C, and melting endotherms were observed between 53 and 57°C for PEO samples. Transitions arising from the cross-linked polymer may be greatly broadened from the ensemble effect of a distributed range of transitions, with some fraction at low cross-link densities providing the measured sharp transitions. A small low-temperature shoulder on the melting endotherm is visible for some cross-linked PEO samples.

Arrhenius plots for polymer–$NaClO_4$ complexes are shown in Figures 3–5. No significant change in conductivities are observed through the temperature range evaluated in the samples with mean cross-link densities of up to 1 mol %.

The apparent dynamic modulus data for each sample were plotted as master curves, according to the time–temperature superposition principle.[15]
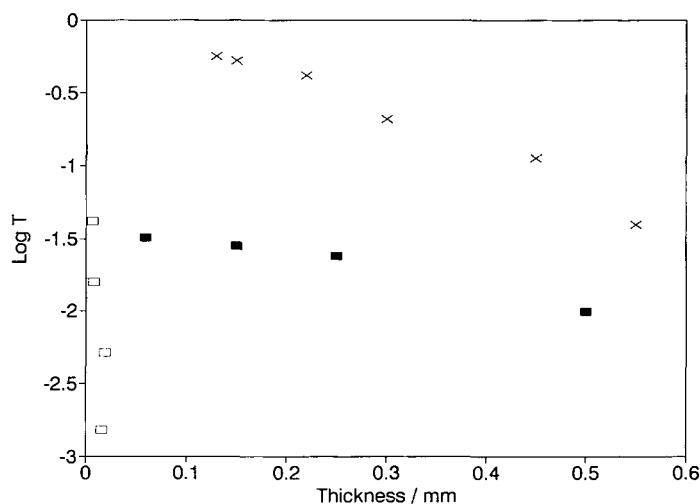

Figure 2 Log (transmittance) at 254 nm vs. sample thickness for (■) PEO, (×) PEM, and (□) PEM containing 0.5 mol % benzophenone.

Table I Sample Compositions, Irradiation Times, Volume Increase by Water Swelling, and Mean Cross-link Densities Determined Using the Flory–Rehner Relation[12]

Sample No.	Composition	Irradiation Time (h)	Volume Increase	Mean Cross-link Density	
				(Mol/L)	(Mol %)
1	PEO	1.0	Soluble	—	—
2	PEO	1.7	79	0.0006	0.008
3	PEO	30	35	0.0091	0.033
4	PEO	66	5.1	0.57	2.1
5	PEM	24	40	0.007	0.03
6	PEM	48	35	0.009	0.04
7	PEO + 0.5% BzPh	0.08	3.8	1.2	4.5
8	PEO + 0.5% BzPh	0.75	3.5	1.5	5.5
9	PEO + 0.5% BzPh	5	3.3	1.8	6.6
10	PEO + 0.5% BzPh	0.08	6.3	0.33	1.2
11	PEO + 0.5% BzPh	1.0	4.9	0.62	2.2
12	PEO + 0.5% BzPh	6	4.5	0.77	2.8
13	PEO + 0.5% BzPh	31	6.8	0.28	1.0
14	PEM + 0.5% BzPh	0.75	Soluble	—	—
15	PEM + 0.5% BzPh	3	16	0.045	0.31
16	PEM + 0.5% BzPh	6	12	0.074	0.39
17	PEM + 0.5% BzPh	13	9.4	0.13	0.52

Curves of the shear storage modulus, G', and the shear loss modulus, G'', vs. angular frequency, ω, measured at different temperatures can be superimposed on curves measured at one temperature by plotting $b_T G'$ and $b_T G''$ vs. $a_T \omega$, where the shift factors a_T and b_T depend only on temperature. The factor b_T is defined as $T_0 \rho_0 / T \rho$, where T is the mea-surement temperature; T_0, the reference temperature; ρ, the density at the measurement temperature; and ρ_0, the density at the reference temperature. The factor a_T is chosen so that curves measured at different temperatures superimpose with the curve measured at the reference temperature. The temperature dependence of the density was neglected
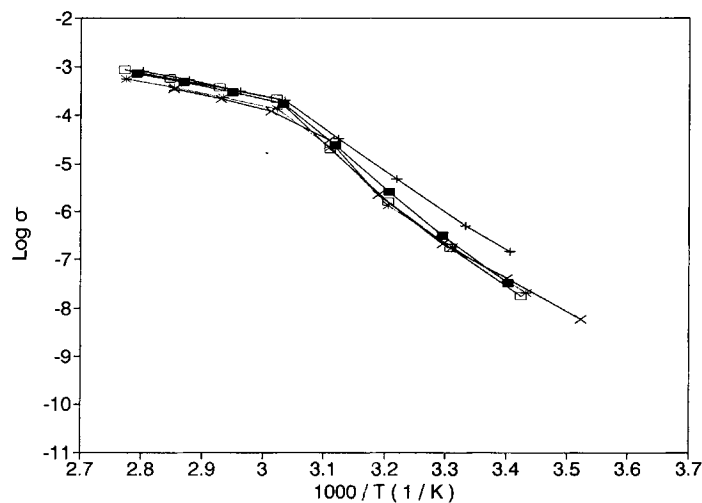

Figure 3 Arrhenius plots for $PEO_{15}NaClO_4$ prepared from irradiated PEO samples (□) **1**, (+) **2**, (*) **3**, and (×) **4**.
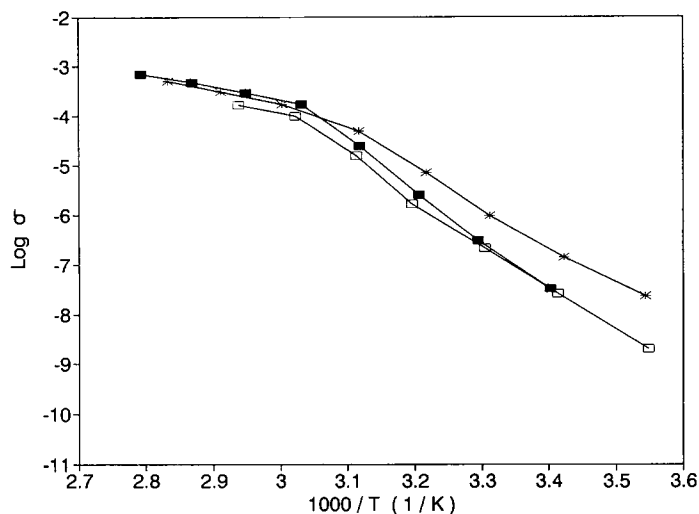
Figure 4 Arrhenius plots for $PEO_{15}NaClO_4$ prepared from (■) unirradiated PEO and irradiated PEO + benzophenone samples (□) **12**, and (*) **13**.

here, since the ratio ρ_0/ρ is very close to unity and b_T was calculated as the ratio of absolute temperatures.

The extent of cross-linking within the samples varies through the thickness, since most (more than 99%) of the UV radiation is absorbed by the films. The dynamic modulus will also vary through the thickness, and the reciprocal of the measured, or apparent, modulus will be the reciprocal of the actual modulus integrated though the thickness of the film. A soft layer at the sample center will therefore tend to dominate the measurements, and the actual de-

pendence of modulus on the extent of cross-linking will be suppressed. Although the actual modulus is not measured in heterogeneous samples, liquid behavior can still be readily distinguished from solid behavior. Apparent modulus values reported here are computed from the measured torques and average strains.

The apparent storage modulus of linear and cross-linked PEO samples is shown in Figure 6, and the apparent loss modulus is shown in Figure 7. The open symbols show modulus for the linear PEO, and the closed symbols denote the values for PEO after
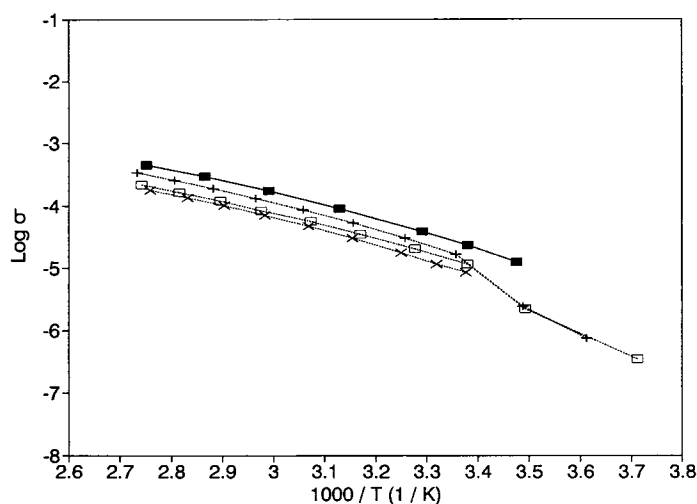

Figure 5 Arrhenius plots for $PEM_{50}NaClO_4$ prepared from (■) unirradiated PEM and irradiated PEM + benzophenone samples (+) **15**, (□) **16**, and (×) **17**.
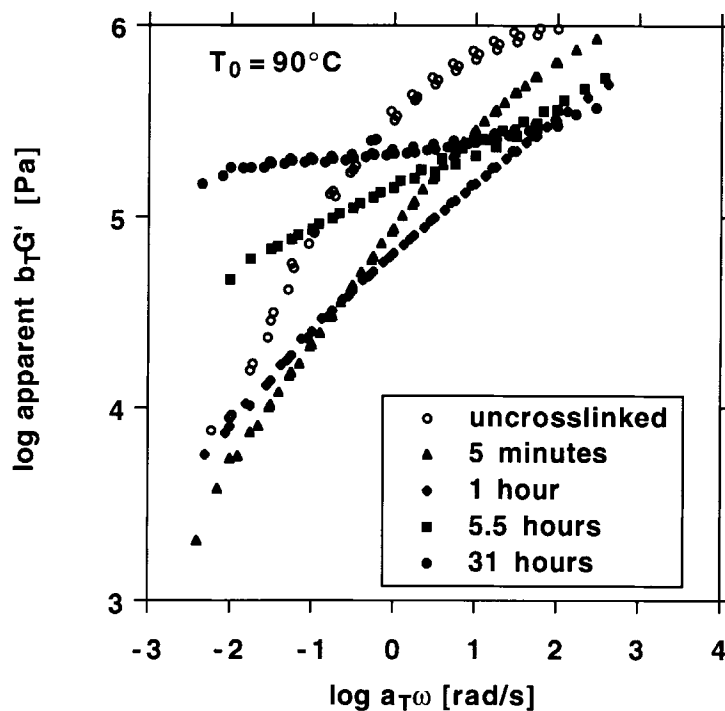
Figure 6 Apparent shear storage modulus for (O) unirradiated PEO, and samples irradiated for (▲) 5 min, (♦) 1 h, (■) 5.5 h, and (●) 31 h. Curves measured at different temperatures are shifted to the reference temperature of 90°C.
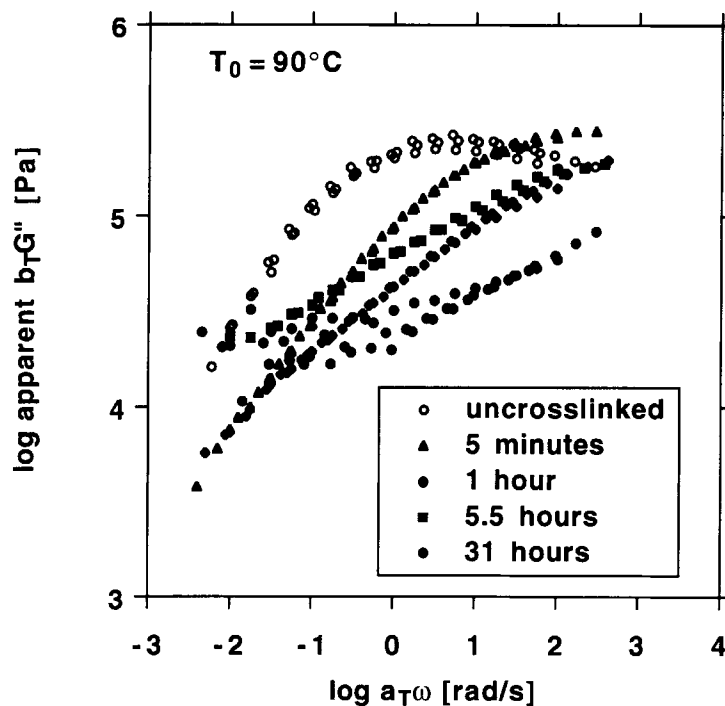

Figure 7 Apparent shear loss modulus for (O) unirradiated PEO, and samples irradiated for (▲) 5 min, (♦) 1 h, (■) 5.5 h, and (●) 31 h. Curves measured at different temperatures are shifted to the reference temperature of 90°C.

irradiation for the times indicated. With short irradiation times, the apparent storage and loss moduli decrease. This may be due to chain scission, which occurs simultaneously with cross-linking. For irradiation times longer than 1 h, the storage modulus increases, especially at low frequencies, consistent with network formation. After 31 h, the apparent storage modulus shows a low-frequency plateau or only a very slight frequency dependence. Contrary to the degree of cross-linking as measured by swelling, the dynamic modulus data indicate that upon irradiation the PEO initially undergoes softening, then cross-links into a network, with a monotonic increase in cross-linking with increasing irradiation time. With sufficient cross-linking, the PEO becomes a stiff elastomer (above its crystalline melting point). Measurement of the dynamic modulus of PEO below the crystalline melting point was not possible as the modulus was too high (above 10^6 Pa) for these thin samples.

The apparent storage modulus of linear and cross-linked PEM samples is shown in Figure 8, and the apparent loss modulus, in Figure 9. The open symbols denote the values for linear PEM, and the closed symbols, for PEM after irradiation. Upon irradiation, both the apparent storage and loss moduli increase at low frequencies and become less frequency-dependent. These observations are consistent with a broadening of the molecular weight and very light cross-linking.

The temperature dependence of the apparent dynamic modulus, given by the temperature dependence of the shift factor, a_T, is evident in Figures 10 (PEO) and 11 (PEM). The shift factor (and hence, the apparent modulus) obeys an Arrhenius temperature dependence over the temperature range studied. Activation energies for flow vary somewhat with irradiation time, as shown in Table II. These energies cannot be easily related to the extent of cross-linking because of the heterogeneous nature of the sample disks.

The mechanistic details of the photochemical reactions that occur in these systems is not well understood; however, some mention is worthwhile in describing the types of cross-links that may be formed. The photochemistry of polyethers is thought to initiate with the homolytic scission of C—O as has been demonstrated in the irradiation of short-chain ethers[16] and polyethers[17] with UV light:

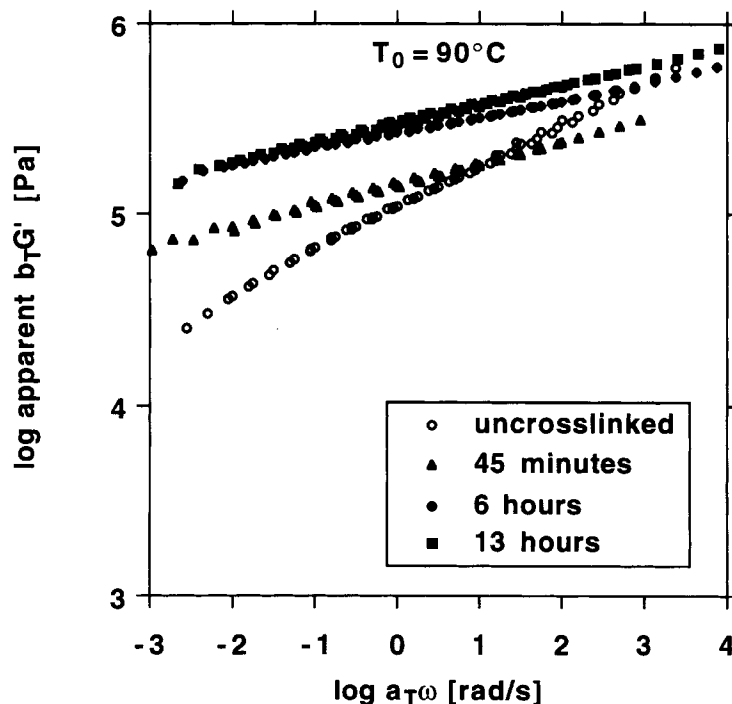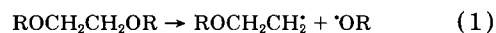$$ROCH_2CH_2OR \rightarrow ROCH_2CH_2^. + {}^.OR \qquad (1)$$

Figure 8   Apparent shear storage modulus for (O) unirradiated PEM, and samples irradiated for (▲) 45 min, (◆) 6 h, and (■) 13 h. Curves measured at different temperatures are shifted to the reference temperature of 90°C.
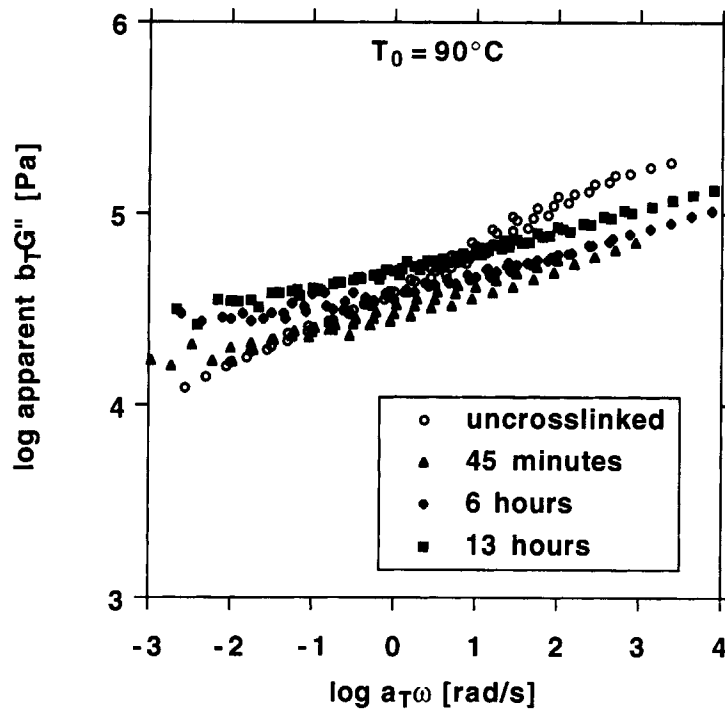
Figure 9 Apparent shear loss modulus for (O) unirradiated PEM, and samples irradiated for (▲) 45 min, (♦) 6 h, and (■) 13 h. Curves measured at different temperatures are shifted to the reference temperature of 90°C.

The chemistry following this initial event can be complex, and many possible routes are feasible: The radicals generated may undergo intramolecular rearrangement, producing unsaturated groups, or may interact with other polymer chains. Two such direct cross-link forming steps are
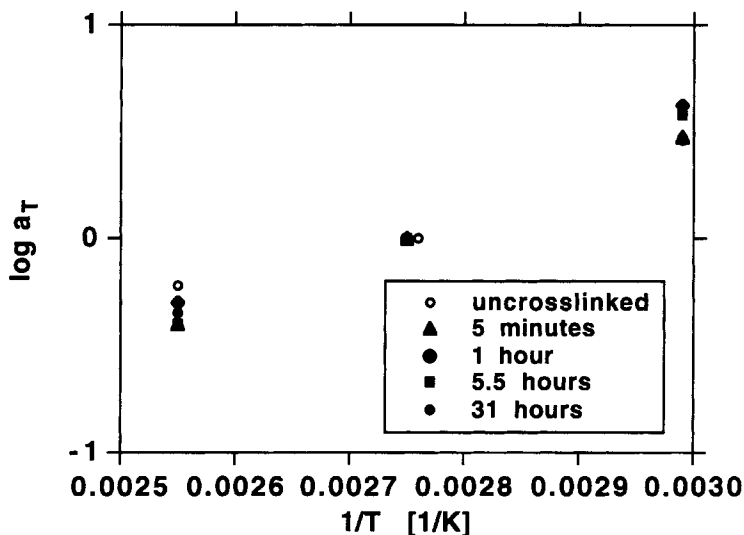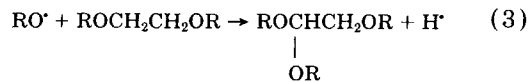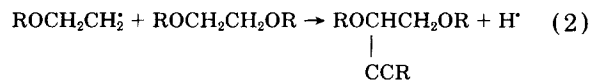
$$ROCH_2CH_2^{\cdot} + ROCH_2CH_2OR \rightarrow ROCHCH_2OR + H^{\cdot} \quad (2)$$
$$| $$
$$CCR$$

$$RO^{\cdot} + ROCH_2CH_2OR \rightarrow ROCHCH_2OR + H^{\cdot} \quad (3)$$
$$|$$
$$OR$$

Figure 10 Arrhenius plots of the shift factor a_T from the dynamic modulus of (O) unirradiated PEO, and samples irradiated for (▲) 5 min, (♦) 1 h, (■) 5.5 h, and (●) 31 h.
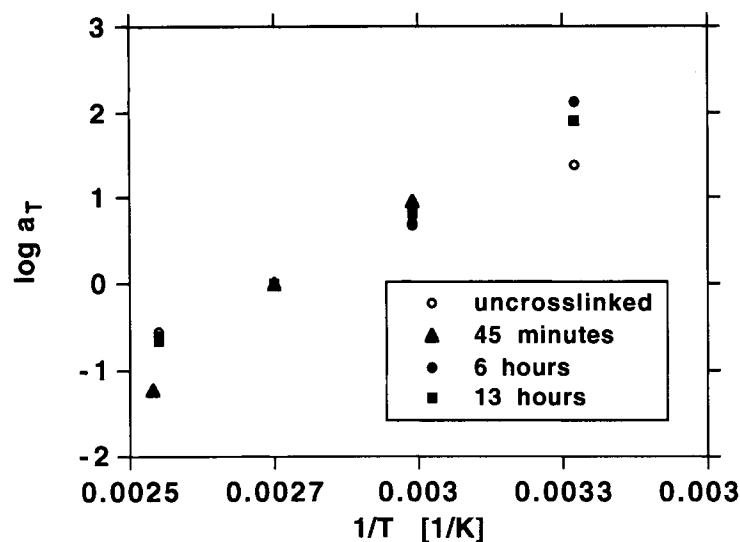
Figure 11   Arrhenius plots of the shift factor a_T from the dynamic modulus of (○) unirradiated PEM, and samples irradiated for (▲) 45 min, (♦) 6 h, and (■) 13 h.

In addition, hydrogen abstraction from other chains may occur:

$$RO^· + ROCH_2CH_2OR \rightarrow ROH + RO\dot{C}HCH_2OR \quad (4)$$

with subsequent rearrangement or reaction of the radical formed. Although a large number of cross-link sites can be generated by the above processes, stable linkages formed should be similar to those in the products from reactions (2) and (3).

^{1}H- and ^{13}C-NMR spectra of even highly cross-linked products do not show new peaks; however, the ^{13}C peaks are sometimes noticeably broadened. This effect may be due to the ensemble effect of multiple cross-link sites or arise from the slow relaxation kinetics in highly cross-linked networks.

Table II   Activation Energies for Irradiated Samples as Determined by Oscillatory Shear

PEO		PEM	
Irradiation Time (h)	Activation Energy (cal/mol)	Irradiation Time (h)	Activation Energy (cal/mol)
0	7,130	0	12,200
0.083	9,090	0.75	22,400
1.0	9,700	6.0	17,000
5.5	10,200	13.0	16,100
31.0	8,630		

The lack of discrete peaks arising from cross-link sites is, however, not atypical, and new, discrete peaks are often absent in cross-linked PEO. Present research in this project involves the characterization of molecular fragments to discern the nature of the cross-link sites.

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