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Determination of Gel Content and Percent Gel in Radiation-Cured Poly(vinyl chloride)–Cross-Linking Monomer Coatings by Combined GPC–LC Techniques

Molly Y. Hellman, Trevor Bowmer, and Gary N. Taylor*

Bell Laboratories, Murray Hill, New Jersey 07974. *Received March 16, 1982*

ABSTRACT: A GPC–LC technique for determining gel content and monomer and polymer content of the gel as well as molecular parameters for ungelled polymer is outlined for use with monomer–polymer mixtures. The method is applied to mixtures of poly(vinyl chloride) (PVC) and trimethylolpropane trimethacrylate (TMPTMA) and three-component mixtures also containing diundecyl phthalate (DUP) plasticizer. All were cured by electron irradiation. Comparison to the conventional Soxhlet extraction technique and gravimetric analysis reveals that gel content for these PVC mixtures is more accurately measured by the GPC–LC technique. The influence of temperature and extraction time are shown to be very important in accurately determining gel content by the GPC method. Precision is aided by using an internal standard. Data obtained are useful in mechanistic studies and correlations of physical and mechanical properties with molecular changes.

Introduction

The determination of gel content for polymers and cross-linked monomer–polymer mixtures and blends provides data by which physical and mechanical properties can be related to the molecular property changes. Generally, such a determination is made by weighing the gel remaining after all soluble components have been removed by solvent extraction.[1] Extraction is accomplished by Soxhlet techniques using hot solvent or by long-term shaking or rapid stirring in a suitable solvent at room temperature. The technique of Purdon and Mate[2] as modified by Rogozinski and Kramer[3] affords a highly accurate means for determining gel content in poly(vinyl chloride). Its drawbacks are the considerable length of time required before data are obtained and the multiplicity of steps needed. These include dissolution, filtration, centrifugation, and drying of polymer recovered. Soxhlet extraction avoids the physical filtration and centrifugation steps. However, it suffers from the single operating temperature demanded by refluxing solvent and the drying process.

Recently, a more simple technique employing gel permeation chromatography (GPC) was applied to gel content analysis of polymers. The first workers[4] analyzed nitrile rubber latexes by directly injecting the latex onto a GPC column. Results were very good for >30% gel content and analysis times were very short (20–30 min). Correspondence of data between standard static analysis and the GPC method was good.

More recently, Ezrin and Brown[5] reported a similar technique useful for a variety of polymers. In this case filtration of the polymer–gel solution was done prior to injection on the columns. Gel content was calculated from the GPC peak area, a calibration curve, and the initial concentration of the sample in the elution solvent.

The present paper reports the extension of the two previous GPC methods to the more complicated case of polymer–cross-linking monomer mixtures. The particular case chosen for study was poly(vinyl chloride) (PVC) mixed with trimethylolpropane trimethacrylate (TMPTMA). Details of curing this mixture by electron irradiation were first discussed by Salmon and Loan.[6] Additional GPC columns were used in this study to permit a sufficient separation between the monomer and an internal standard that was added to help minimize errors induced by injection volume changes. To our knowledge this is the first report of the use of an internal standard in gel permeation and liquid chromatography to obtain absolute concentration data for eluents.

Experimental Section

Materials. Poly(vinyl chloride) was obtained from BFGoodrich and had $\bar{M}_w = 1.61 \times 10^5$ and $P = 3.26$. Trimethylolpropane trimethacrylate was obtained from Ware Chemical Corp. Diundecyl phthalate was used as received from Monsanto. UV-grade tetrahydrofuran (Waters) was used in the extraction experiments and as the chromatographic solvent. CCl_4 was used as received from Mallinckrodt.

Apparatus. Irradiation of molded PVC–TMPTMA samples was conducted with a Dynamitron electron beam accelerator using 1.5-MeV electrons. Currents ranging from 0.4 to 1.0 mA were used. Absorbed doses <5 Mrd were applied to the samples. Irradiations were conducted under nitrogen at 21–23 °C.

GPC analyses were performed with the Waters Model 244 liquid chromatograph. Most results were obtained with refractive index detection. For some runs UV detection was used for TMPTMA and PVC to which TMPTMA had grafted. The column set consisted of six μ-Styragel columns having porosities of 10^6, 10^5, 10^4, 10^3, 500, and 100 Å. The latter two columns were necessary to obtain good separation between TMPTMA, a large molecule, and CCl_4, the internal standard, which is small, nonpolar, and spherical. A PDP8 Lab 8/E minicomputer was used for data

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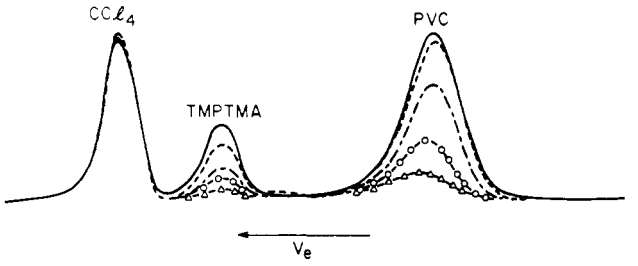

Figure 1. Gel permeation chromatograms of a 2:1 mixture by weight of PVC and TMPTMA in THF using CCl_4 internal standard. Each curve is for a different radiation dose: (—) 0, (---) 0.1, (-·-) 0.5, (○) 1.0, and (△) 3.2 Mrd.

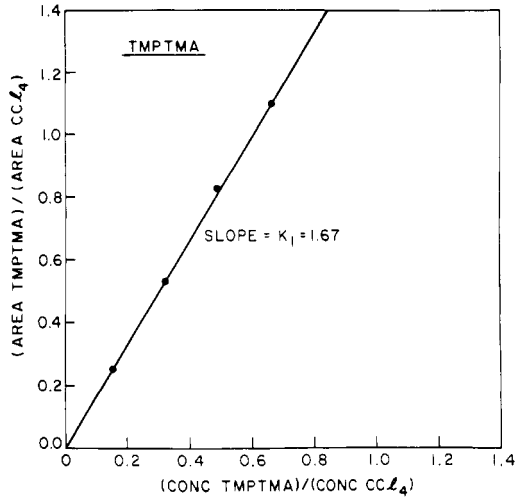

Figure 2. Calibration curve for TMPTMA.

acquisition and reduction. A typical analysis time was 40 min at 2 mL/min.

Sample Preparation. TMPTMA monomer containing a trace amount of thermal stabilizer was added gradually to PVC in a high-speed blender at 60–70 °C. The resulting powders were compression molded in a press at 150–160 °C for 2.5 min to give sheets ranging in thickness from 100 to 400 μm. Samples having PVC/TMPTMA nominal ratios of 10:1, 4:1, 2:1, and 1:1 were prepared. Accurate component percentages were determined by GPC and chlorine elemental analysis. Identical procedures were used for the three-component mixtures.

Gel Content Analysis. Static gel content analyses were determined by Soxhlet extraction. An irradiated blend (1–2 g) was placed in a weighed cellulose thimble and extracted for 20–25 h with refluxing THF. The temperature in the thimble during the Soxhlet cycle varied from 63.5 to 65.0 °C, a few degrees below the boiling point of THF (67 °C). The insoluble material remaining after drying for 1 h at 60 °C was weighed. It is defined as the gel content for the sample.

GPC-LC Method. For the GPC analyses 125 mg of each molded sample was placed in a 25-mL volumetric flask. THF (20 mL) was added. The capped sample was heated at a given temperature for 17 h. The solution was stirred continuously by a tiny magnetic spin bar. After the solution cooled to room temperature, the spin bar was removed. Two milliliters of a 0.5% by volume solution of CCl_4 in THF was added followed by additional THF until the mark was reached. The solution was filtered through a 0.45-μm sintered Ag filter. A 200-μL aliquot of this solution was injected into the GPC. The flow rate was 2 mL/min.

From each resulting GPC chromatogram three well-defined peaks having base line separation were obtained. A typical chromatogram is shown in Figure 1. The area of the PVC and TMPTMA peaks is a direct measure of the soluble portion of the irradiated sample. Areas were calculated by computer using a program that determines the Schultz distribution for each peak. The CCl_4 internal standard area was used to normalize the PVC and TMPTMA areas in order to minimize errors due to injection volume changes. CCl_4 was the only standard we investigated that

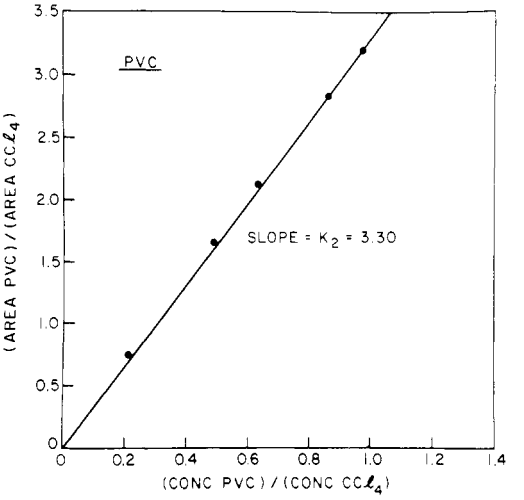

Figure 3. Calibration curve for PVC.

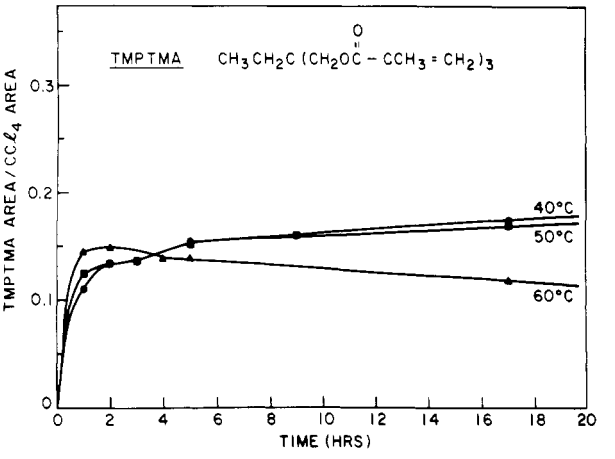

Figure 4. (TMPTMA area)/(CCl_4 area) vs. extraction time in hours at three temperatures: (●) 40 °C; (■) 50 °C; (▲) 60 °C.

exhibited base line separation from the TMPTMA peak. Any peak overlap causes unacceptable errors in peak area. These result mainly from failure to make a systematic estimation of when one peak ends and the other begins.

To obtain absolute component concentrations from the peak area, calibration curves were obtained using unirradiated samples of TMPTMA, PVC, DUP, and CCl_4. Figures 2 and 3 show the calibration curves for TMPTMA and PVC, respectively. Both plots are linear as expected and pass through the origin.

Results and Discussion

Before analyzing irradiated samples, we used the GPC–LC analysis method to determine the optimum temperature and time for the solvent extraction. Three temperatures were studied: 40, 50, and 60 °C. The latter most nearly approximates the conditions in the classic Soxhlet extraction method where the average temperature was about 64 °C. The sample we studied contained 2 parts of PVC and 1 part of TMPTMA. It had been irradiated to a dose of 0.61 Mrd. The results are presented in Figure 4 for TMPTMA and Figure 5 for PVC. THF was the extracting solvent. Initial dissolution rates are faster for both materials at the higher temperatures. For TMPTMA, however, extraction times longer than 2–3 h at 60 °C resulted in disappearance of material. At 17 h 16% of the maximum TMPTMA extracted at 3 h had been lost, presumably by thermally induced polymerization. TMPTMA extractions at 40 and 50 °C were virtually identical after 2 h of extraction time. At 17 h the extractions appear complete. The value obtained at 60 °C for 17 h is only 69% of the maximum value at 50 °C. The

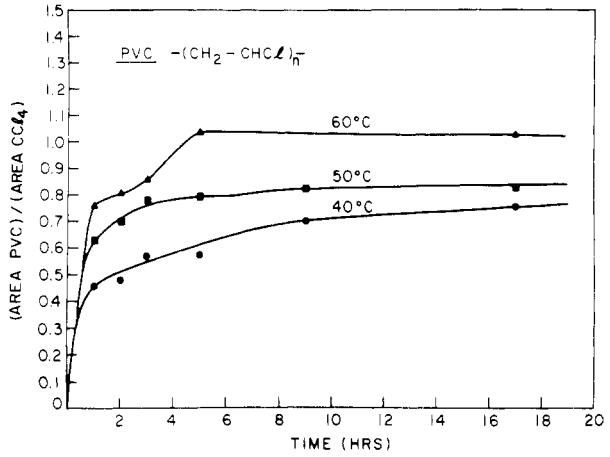

Figure 5. (PVC area)/(CCl_4 area) vs. extraction time at three temperatures as in Figure 4.

Table I
Peak Areas and Area Ratios for PVC and TMPTMA in a 2:1 Blend Irradiated to 0.61 Mrd and Extracted at Various Temperatures with THF

dissolution time, h	area			area ratio	
	PVC	TMPTMA	CCl_4	PVC / CCl_4	TMPTMA / CCl_4
			40 °C		
1	983	268	2117	0.464	0.127
2	1009	281	2107	0.478	0.134
3	1187	276	2030	0.584	0.136
5	1247	342	2143	0.582	0.160
17	1524	349	2012	0.757	0.173
			50 °C		
1	1331	258	2104	0.632	0.113
2	1455	283	2076	0.700	0.136
3	1626	286	2085	0.780	0.137
5	1707	298	2180	0.783	0.137
9	1757	351	2176	0.807	0.161
17	1757	362	2100	0.836	0.172
			60 °C		
1	1537	299	2028	0.758	0.147
2	1871	312	2123	0.881	0.147
4	1860	292	2177	0.854	0.137
5	2175	290	2098	1.036	0.133
17	2235	263	2170	1.029	0.121

most favorable extraction conditions for TMPTMA are 50 °C for 17 h.

PVC extraction is more efficient at higher temperature. In Figure 5 we see that at 60 °C the more efficient (faster) extraction at short times is enhanced at intermediate times. At 17 h there seems to be a slight loss of PVC (presumably by reaction). At 50 °C the extraction appears to be complete at 17 h whereas extraction is still continuing at 40 °C and 17 h. Thus there appears to be a PVC component in the irradiated mixture that is not soluble below 50 °C. It constitutes about 20% of the total soluble PVC. The best conditions for solubilizing PVC would appear to be 5–8 h at 60 °C.

In conducting our analyses of irradiated materials, we used an extraction time of 17 h at 50 °C. We were certain that no degradation was occurring under these conditions. By correcting the PVC data to the 60 °C values, we could get more accurate gel content data if we desired. Finally, 17 h is a convenient overnight heating time. If prolonged heating occurred, the samples would not change appreciably at 50 °C.

The role and importance of the internal standard are evident in the data summary given in Table I for the extraction experiments just described. Note that the CCl_4

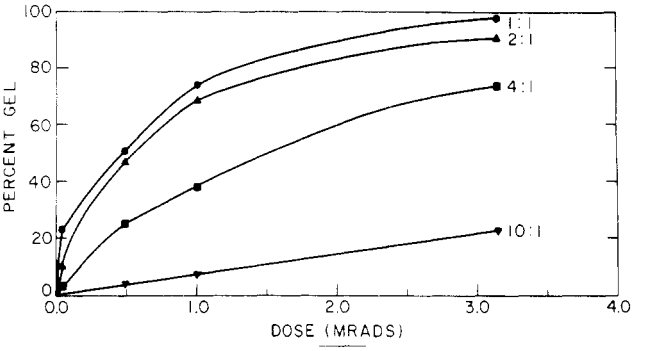

Figure 6. Percent gel determined by GPC vs. dose for four PVC/TMPTMA mixtures: (●) 1:1; (▲) 2:1; (■) 4:1; (▼) 10:1.

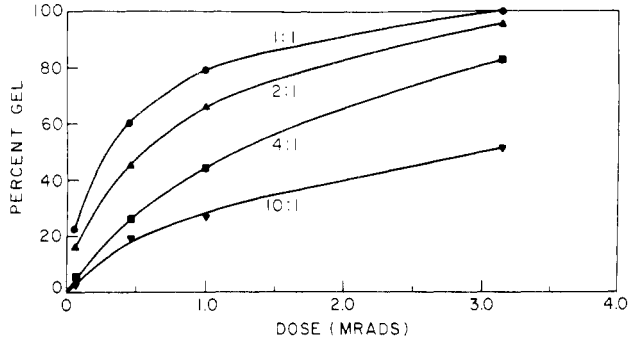

Figure 7. Percent gel determined by the Soxhlet method vs. dose for four PVC/TMPTMA mixtures as in Figure 6.

standard peak area varies by ±5%. Some of this is attributable to imprecise base line estimation but most is due to injection volume variations. Gel content calculation using the peak area ratios and the calibration curve is estimated to have a precision of ±3%. We are confident that the small changes observed at long extraction times in Figures 4 and 5 are real.

Percent gel is calculated in the following way. From the slopes K_1 and K_2 of the calibration curves, the measured area ratios, and the concentration of the internal standard, the soluble concentrations of TMPTMA and PVC are first calculated.

$$S_{\text{TMPTMA}} = \frac{(\text{conc of } CCl_4) \times (\text{area ratio})_{\text{TMPTMA}}}{K_1} \quad (1)$$

$$S_{\text{PVC}} = \frac{(\text{conc of } CCl_4) \times (\text{area ratio})_{\text{PVC}}}{K_2} \quad (2)$$

The percent gel is then given by

$$\%\ \text{gel} = \frac{(\text{conc of sample}) - (S_{\text{TMPTMA}} + S_{\text{PVC}})}{\text{conc of sample}} \quad (3)$$

In the radiation studies we have determined the percent gel and the percent of each component in the gel by this GPC–LC method for four different PVC/TMPTMA compositions. By weight these were 1:1, 2:1, 4:1, and 10:1. Duplicate and sometimes triplicate determinations were conducted for each sample which had been irradiated to a known dose given in Mrds. In Figure 6 we summarize the percent gel data. All values were not corrected for that additional amount of PVC which would have been soluble had the extraction been conducted at 60 °C. Correction would shift each curve to lower percent gel values. Note that with the exception of the 10:1 sample, each sample showed a nonlinear dependence of percent gel on electron dose. Gelation is most facile at high TMPTMA content.

It is instructive to compare the curves in Figure 6 with those obtained using the conventional Soxhlet extraction

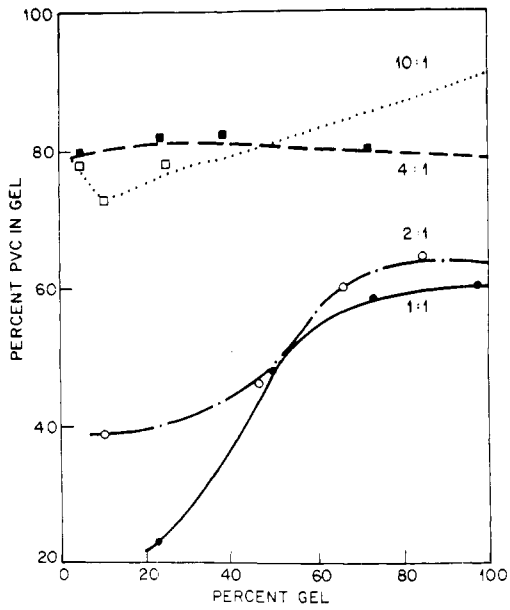

Figure 8. Percent PVC in the gel vs. percent gel for four PVC/TMPTMA mixtures.

method. We show typical curves for the latter in Figure 7. With the exception of the 2:1 curves, the Soxhlet method affords higher percent gel values. This occurs even though this higher temperature extraction would be expected to yield lower percent gel due to more efficient PVC solubilization. Differences between the two methods are greatest for the high-PVC-content samples. As an example, the curve for the 10:1 sample is linear in Figure 6 but nonlinear in Figure 7. Percent gel at 17 h for the 3.2-Mrad-dose samples is 100, 96, 83, and 52% with the Soxhlet method for the 1:1, 2:1, 4:1, and 10:1 compositions, respectively, compared to 98, 91, 74, and 23%, respectively, for the 50 °C extraction.

Thus, the Soxhlet extraction appears less efficient in extracting soluble material and gives less accurate values for gel content. We suspect that three factors contribute to this inefficiency: (1) the static (unstirred) condition during dissolution; (2) the large volume of material required; (3) clogging of the extraction thimble.

In addition to gel content and percent gel, the GPC–LC analysis also provides data from which percent cross-linked monomer and percent cross-linked polymer in the gel can be calculated. This is helpful in correlating physical property changes with degree of cross-linking, amount of free monomer in the mixture, and amount of free PVC. In Figure 8, percent PVC in the gel is plotted vs. percent gel for the four mixtures as a function of radiation dose. From such plots we see that the efficiency of PVC incorporation into the gel varies with both composition and radiation dose. Generally, at low doses less PVC is locked. These results should of course vary with PVC molecular weight; however, we have not investigated this aspect here. At high doses often a reverse trend is observed, which may alter this dependence.

In addition to the previous gel data, GPC–LC analysis provides other useful information. Analysis of unirradiated samples, which is required to obtain an initial concentration, also provides data on actual composition. These data are summarized in Table II. Corrections for the higher temperature extraction are not applicable since all four samples were completely soluble in THF. The agreement between actual and desired values was excellent for the 10:1 and 4:1 samples having high PVC content. Some discrepancy was observed for the 2:1 sample and became larger as TMPTMA content increased such that a 20% error was evident for the 1:1 sample. These discrepancies may result from incompatibility at high TMPTMA concentrations and monomer loss during blending. The actual compositions determined by GPC–LC were used to calculate gel content and percent gel. The near coincidence of the 1:1 and 2:1 curves in Figure 6 thus reflects the nearly identical starting compositions.

Table II
Desired and Actual Compositions for Electron-Irradiated Blends

sample type	desired % PVC	desired % TMPTMA	actual % PVC	actual % TMPTMA
1:1	50.0	50.0	60.0	40.0
2:1	66.6	33.4	63.2	36.8
4:1	80.0	20.0	79.7	20.3
10:1	90.9	9.1	90.6	9.4

Table III
Effect of Radiation Dose on Molecular Parameters and Percent Gel

electron dose, Mrd	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	P	% gel
	1:1 Composition			
0.0	0.588	1.962	3.34	0
0.1	0.678	1.780	2.63	23
0.5	0.415	1.064	2.56	50
1.0	0.543	1.073	2.01	74
3.2	0.554	0.795	1.44	98
	2:1 Composition			
0.0	0.496	1.633	3.29	0
0.1	0.510	1.516	2.97	10
0.5	0.441	1.331	3.01	47
1.0	0.365	0.987	2.70	69
3.2	0.316	0.870	2.75	91
	4:1 Composition			
0.0	0.543	1.630	3.00	0
0.1	0.524	1.692	3.23	3
0.5	0.683	1.891	2.77	25
1.0	0.507	1.519	3.00	38
3.2	0.353	0.867	2.46	74
	10:1 Composition			
0.1	0.546	1.623	2.97	0
0.5	0.590	1.820	3.08	4
1.0	0.535	1.905	3.56	7
3.2	0.490	2.506	5.11	23

Another set of data we measure are $\bar{M}_n$, $\bar{M}_w$, and P values for PVC. The molecular weight values reported here are given in units of polystyrene equivalent molecular weight. The results are presented in Table III along with percent gel data. Certain general comments are noteworthy. First, $\bar{M}_n$ values are relatively unaffected by irradiation except at the highest doses, where a drop is generally observed. The most drastic changes occur for $\bar{M}_w$ values. For the 1:1, 2:1, and 4:1 compositions a 3.2-Mrad dose leads to a two-fold reduction of $\bar{M}_w$. Since $\bar{M}_n$ is relatively invariant, the polydispersity P decreases with increasing dose. The abnormally low P value for the 3.2-Mrad 1:1 sample likely results from difficulty in measuring the small amount of soluble PVC accurately. Of all the series, the 10:1 composition behaves quite differently. This is reflected by the increase in molecular weight with dose and a corresponding broadening of the molecular weight distribution, which results primarily from increases in $\bar{M}_w$. This is indeed what is expected to occur if branching reactions begin to compete effectively with the cross-linking processes, which dominated at higher TMPTMA concentrations.

Branching is indicated when using the UV detector during a typical GPC–LC analysis. In Figure 9 we show

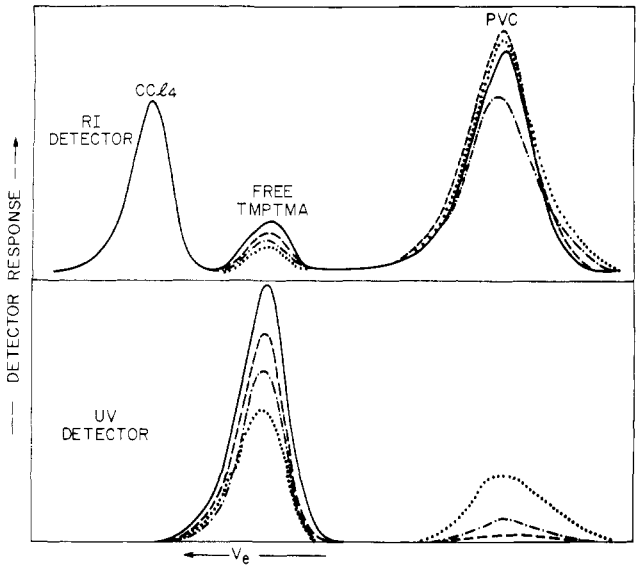

Figure 9. GPC chromatographic traces for the 10:1 PVC/TMPTMA mixture obtained using RI and UV detection. Samples were irradiated to 0 (—), 0.5 (– – –), 1.0 (– · –), and 3.2 (· · ·) Mrd.

typical chromatographic traces obtained for the 10:1 mixture irradiated to various doses. The upper curves were obtained with the RI detector. Note the presence of absorption for all peaks. In the lower part of the figure we show typical traces obtained for the same samples but using the UV detector. The traces for UV detection show a strong peak for TMPTMA and a moderate peak at the point of PVC elution. Note that the intensity of the TMPTMA peak decreases with irradiation dose but that the UV peak for PVC increases with dose and is zero at zero and very low doses. Since TMPTMA has three UV-absorbing reactive double bonds, we surmise that ≥1 and <3 of the active groups per TMPTMA molecule are branched to the PVC backbone. This reaction is favored by the high PVC concentration since no similar peaks are found by UV detection in the 4:1 sample. High concentration favors creation of reactive sites on the PVC backbone. At lower PVC concentrations presumably the phase is mobile enough to permit more facile cross-linking through the TMPTMA molecules.

Extension to Three Components. Usually in these coatings a third component (plasticizer) is added. We have shown that this technique can be extended to a three-component system. The chromatograms in Figure 10 show the separation of PVC, TMPTMA, and diundecyl phthalate (DUP). Note that unlike TMPTMA and PVC, DUP is not bound to the polymer upon electron radiation to a dose of 4.64 Mrd. UV absorption in the PVC region shown in Figure 9 is eliminated when DUP is present.

Conclusions

In this paper we have shown that monomer–polymer mixtures that are cross-linked by actinic radiation may be analyzed conveniently and precisely by GPC–LC techniques. The precision results from the GPC method itself and the use of an internal standard to correct for nonuniform injection size. Using a simple solvent extraction technique, we are able to obtain fairly precise (±3%) values for gel content and percent gel. We find for the PVC–TMPTMA case that extraction temperature and time are critical to obtaining accurate measurements. At 60 °C PVC is most efficiently extracted while 50 °C is optimum for TMPTMA. Gel content and percent gel as measured by the GPC–LC technique are more accurate than obtained by the Soxhlet method of extraction, which tends to overestimate percent gel. Conventional molecular weight data can also be readily obtained from the elution curves. Comparison of elution curves obtained using refractive index and UV detectors coupled with the molecular weight data can be useful in deriving an understanding of the molecular processes involved. A more detailed discussion of these analyses and correlation with physical and mechanical properties of these blends will be discussed elsewhere.[7]

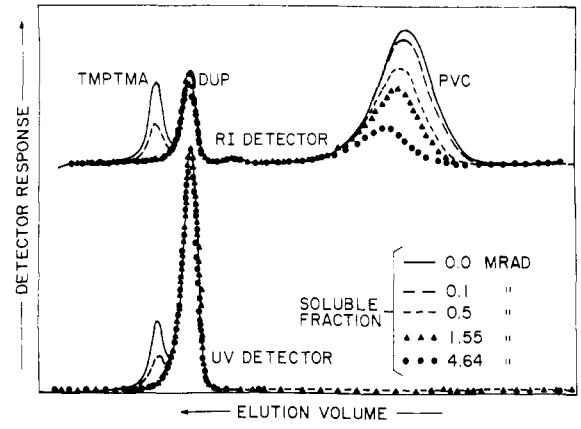

Figure 10. The equivalent to Figure 9 for a three-component system consisting of PVC, TMPTMA, and DUP using CCl_4 as the internal standard. Samples were irradiated to 0 (—), 0.1 (– – –), 0.5 (- - -), 1.55 (▲), and 4.64 (●) Mrd.

Registry No. PVC, 9002-86-2; TMPTMA, 3290-92-4; DUP, 3648-20-2.

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