

Synthesis of Transparent Fluorocarbon Elastomers: Effect of Crosslinker Type and Electron Beam Irradiation Level on Physical and Mechanical Behavior

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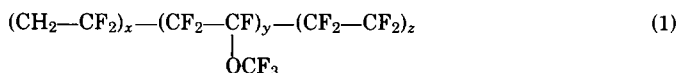
Synopsis

Saturated fluorocarbon elastomers are very resistant to chemical reactions, including those of a crosslinking nature. In order to study proper methods of preparing these materials, Viton GLT was mixed with various levels of trimethylol propane trimethacrylate, TMPTM, and triallyl isocyanurate, Diak #7. After molding, the materials were subjected to electron beam irradiation. The glass transition, rubbery modulus, viscoelastic behavior, and equilibrium swelling were used to characterize the materials as a function of crosslinker and irradiation level. In general, the modulus and gel fraction increased with both crosslinker content and irradiation level. Mixtures of both crosslinking monomers produced an unexpected synergism, yielding higher tensile strength, and earlier onset of gelation.

INTRODUCTION

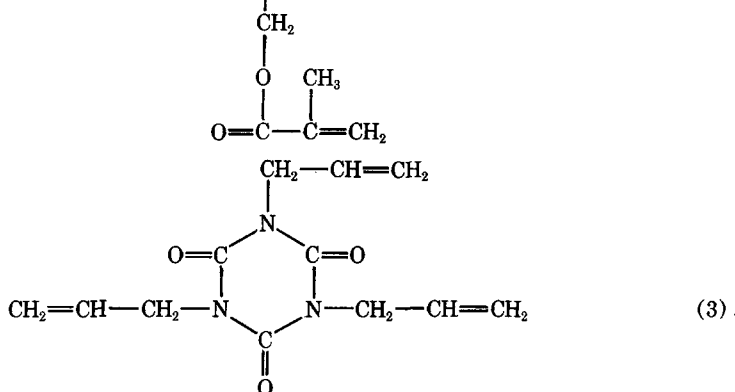
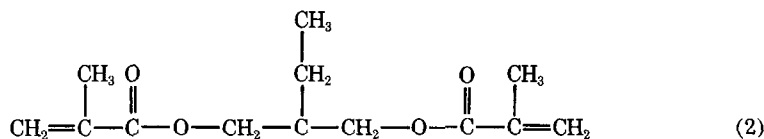
Saturated fluorocarbon elastomers stand out for their inertness and resistance to chemical reactions, including those of a crosslinking nature. The problem of preparing properly crosslinked materials is magnified if transparency is required, for then a range of fillers or basic compounds,¹ which can react with hydrogen fluoride are ruled out. This problem was attacked through the use of multifunctional crosslinking monomers and electron beam irradiation.

Viton GLT,² a copolymer of vinylidene fluoride, perfluoro(methyl vinyl ether) and tetrafluoroethylene,³ served as the starting elastomer. It has the approximate composition



where $x = 4$, $y = 1$, and $z = \text{trace}$. The terpolymer is commercially prepared by emulsion polymerization using peroxide initiators.²

The crosslinking monomers used in this study were the multifunctional compounds trimethylolpropane trimethacrylate (TMPTM), structure (2), and Diak #7 (triallyl isocyanurate), structure (3).



This paper is the second of three devoted to this investigation. The first paper was concerned with Viton A, which has a significantly higher glass transition temperature, and much different chemistry.⁴ The third paper deals with optimizing the synergism obtained, first noted in this paper, when the compounds shown in structures (2) and (3) were judiciously mixed.⁵ Reference 4 reviews the fluorocarbon literature to date.

EXPERIMENTAL

Materials

Viton GLT was obtained from E. I. duPont de Nemours and Co. in milled chunk form. The crosslinking reagents were trimethylolpropane trimethacrylate (TMPTM) obtained from Polysciences and triallyl isocyanurate (Diak #7) obtained from duPont.

Synthesis

The Viton GLT was compounded with 0–10% TMPTM, 0–10% Diak #7, or combinations of both, on either a Brabender or a Farrel rubber mill. Except for frictional heating, no heat was supplied. The samples became homogeneous after 20–25 min. The milled rubber was either (1) compression-molded in a polished steel mold (with or without Mylar film) at 120°C and 20 tons platen pressure in a hydraulic press for 10 min, or (2) transfer-molded by preheating the milled rubber in the transfer cup for 5 min and then injecting it into a polished steel mold at 50–80 tons platen pressure through a $\frac{3}{8}$ in. orifice.

The molded samples were taken to an electron beam sources at Radiation Dynamics, Inc. or Columbia Research Corporation and irradiated at 0–20 Mrads. A megarad (Mrad) is defined as a unit of energy absorbed from ionizing radiation, equal to 1×10^4 J/kg of irradiated material. The sheets of molded rubber were

placed horizontally on carts which were attached to a conveyer and passed under a 3 million electron volt beam whose current was 25 mA (for 2.5 Mrads). The desired dosage was obtained by varying the cart speed or the current, or by repeating the cycle until the desired dosage was obtained.

Physical and Mechanical Characterization

Stress-strain curves were obtained on a TTDL model Universal Testing Instrument from Instron Engineering Corporation with a 200 lb tensile load cell. Both crosshead speed and chart paper speed were 2 in./min, and sample shapes were based on ASTM D638⁶ type IV (large dogbone) and ASTM D1708⁷ (microtensile specimen). Tensile strength, percent elongation to break, and Young's modulus (E), were determined by this experiment.⁶

The shear modulus at 10 s, $G(10)$, was determined using a Gehman Torsion Stiffness Tester,⁸ raising the temperature 1°C/min. The results are reported as three times the shear modulus ($3G$), which is approximately equal to Young's modulus (E) for elastomeric materials.

Studies of stress relaxation were carried out using the Gehman apparatus with a silicone oil bath. Stress relaxation experiments covered the temperature range -55-100°C. Modulus, $3G(t)$, readings were taken from 3-3000 s at various intervals.

Optical measurements were taken on a Beckman DK double beam spectrophotometer through the visible range to determine the percent transmission. The Brice-Phoenix experiment was executed by placing the sample in silicone oil in a cell and comparing it to a reference cell with just silicone oil. The oil was used to eliminate the effect of surface defects in the samples by matching refractive indices. The turbidity was calculated using a modified Beer-Lambert Law.

Swelling and extraction studies were performed by placing weighed and measured samples into vials containing a large excess of acetone. After equilibrium was reached, the extracted samples were reweighed and remeasured, placed in a vacuum to remove solvent, and weighed and measured again, to determine the extent of swelling and the sol fraction. Differential scanning calorimetry, DSC, was performed with a Perkin-Elmer (DSC-1B). Differential Scanning Calorimeter, to determine the glass transition temperatures.

RESULTS

Viton GLT, molded as received, forms a pale yellow, transparent elastomer. Naturally, a significant amount of creep is apparent on handling. The following experiments characterize the material before and after several series of crosslinking studies. Except where specifically mentioned, the original transparency was retained.

Glass Transition Behavior

Figure 1 illustrates the modulus-temperature behavior of a 1.5% TMPTM/5 Mrad sample of Viton GLT. The glass transition temperature, T_g , for this sample was determined to be -42°C. By way of comparison, a Viton A sample similarly crosslinked had a T_g of -20°C.⁴

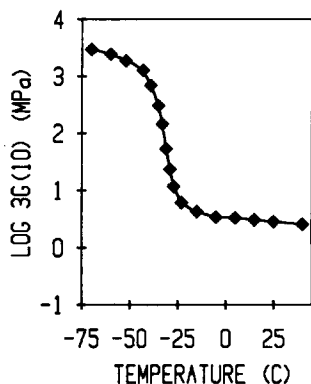


Fig. 1. Viton GLT at 1.5% TMPTM/5 Mrad: modulus vs. temperature behavior.

Glass transition temperatures for several materials are given in Table I, which include determinations from modulus-temperature curves (Gehman) and from differential scanning calorimetry (DSC) measurements. A slight increase in the glass transition temperature is seen for increasing TMPTM concentration, as predicted by theory.^{9,10} The glass transition for the mixed crosslinker sample, 1.5% TMPTM/1.5% Diak #7/3 Mrad, was obtained from a master curve (see Fig. 4 below).

Rubbery Modulus

At low radiation doses, the modulus increases with dose (see Fig. 2). Then the modulus reaches a maximum and declines, as the sample begins to degrade.

According to rubber elasticity theory,¹¹ the shear modulus of an elastomer is directly proportional to the number of active network chains per unit volume, n :

$$G = nRT \quad (4)$$

where R represents the gas constant and T the absolute temperature. Values of the quantity n are shown in Table II for a range of experimental conditions. Values of n increase with the concentration of TMPTM, as expected, but apparently have already reached a maximum value for the Diak #7, under the conditions shown.

TABLE I
Glass Transition Behavior of Crosslinked Viton GLT

Sample	Gehman T_g (°C)	DSC T_g (°C)
Linear polymer	—	-42
0%/5 Mrad	—	-41
1% TMPTM/7.5 Mrad	—	-43
1.5% TMPTM/5 Mrad	-42	—
3% TMPTM/5 Mrad	-35	—
3% Diak #7/7.5 Mrad	-36	-39
1.5% TMPTM/1.5% Diak #7/3 Mrad	-39 ^a	—

^a From Master Curve.

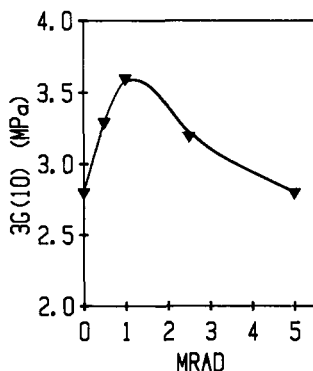


Fig. 2. Viton GLT, 1.5% TMPTM: effect of irradiation level on the shear modulus behavior.

Stress Relaxation and the WLF Equation

Stress relaxation data on Viton GLT (1.5% Diak #7/1.5% TMPTM/3 Mrad) were obtained as a function of time at different temperatures (Fig. 3). Three regions of behavior may be identified: (1) the glassy region, -40°C and below, (2) the glass-transition region, -40°C – -25°C , where the onset of coordinated molecular motion predominates, and (3) the rubber region, -25°C and above. There is little relaxation in this range, indicating a reasonable degree of cross-linking.

TABLE II
Active Network Chains in Viton GLT Materials Network Chains ($\text{mol}/\text{cm}^3 \times 10^{-4}$)

Crosslinker and level	Irradiation level (Mrad)			
	0	2.5	5	7.5
None	3.12	3.43	2.62	2.58
1% TMPTM	—	3.48	3.01	2.74
2% TMPTM	—	4.32	3.29	3.93
3% TMPTM	—	5.69	5.32	4.39
5% TMPTM	—	5.86	5.31	4.71
3% Diak #7	—	5.68	5.95	6.08
5% Diak #7	—	4.33	5.49	9.18

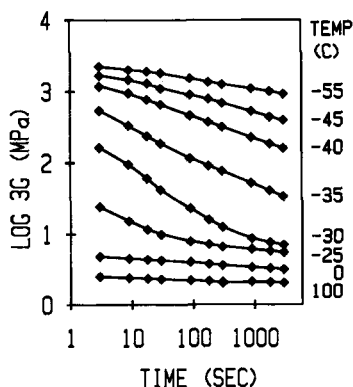


Fig. 3. Stress-relaxation as a function of temperature: Viton GLT (1.5% Diak #7/1.5% TMPTM/3 Mrad).

A master curve was obtained by shifting the curves in Figure 3 along the time axis with respect to a reference temperature, 20°C,^{11,12} using the time-temperature superposition principle, until all fit together to form a single smooth curve (Fig. 4). The shift factor (Fig. 4, insert) was recorded as a function of temperature, and agrees within experimental error up to $T_g + 50$ with shift factors calculated using the WLF equation^{11,12}

$$\log a_t = -17.44(T - T_g)/[51.6 + T - T_g] \quad (5)$$

Again, Figure 4 reflects the three major regions of viscoelastic behavior: glassy, glass-rubber transition, and rubbery. However, time rather than temperature is the major variable. The time necessary for molecular relaxation at 20°C, from Figure 4, is in the range of 10^{-14} – 10^{-11} h.

By crossplotting the data at 10 s as a function of temperature a T_g of -39°C was found (see Table I). Salazar et al.¹³ also reported a master curve for fluoroelastomer materials.

Swelling and Extraction

A modified form of the Flory-Rehner^{11,14} equation was used to calculate the moles of active chains per cm³, n , from fully swollen networks

$$-[\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 n (w_g^{2/3} v_2^{1/3} - 2v_2/F)/w_g \quad (6)$$

where v_2 is the volume fraction of polymer in the swollen gel, w_g is the gel fraction, V_1 is the molar volume of the solvent, χ is the Flory interaction parameter, and F is the functionality of the crosslink site, in this case assumed to be 6 because both TMPTM and Diak #7 are hexafunctional. The quantity χ was determined to be $0.5 \pm .02$.

Swelling and extraction studies were performed on the fluorocarbon elastomers to determine how the quantity n varies with type of crosslinking system and the radiation dose. The results are tabulated in Table III.

The percentage of extractables, Table III, is seen to decrease with increasing radiation dose. At less than 1 Mrad irradiation, large amounts of solubles (33–55%) were found for the 3% Diak #7 system. Somewhat smaller amounts (29–34%) were seen for the 1.5% TMPTM systems. Below 0.5 Mrad, the samples

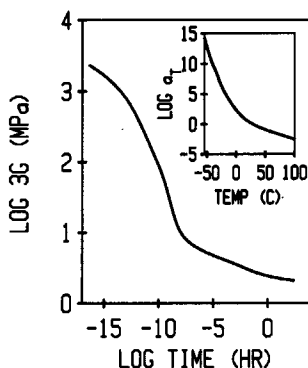


Fig. 4. Viton GLT Master Curve For 1.5% Diak #7/1.5% TMPTM/3 Mrad, prepared by superposition of the data in Figure 2.

TABLE III
 Swelling and Extraction Studies

Mrad	Volume fraction v_2	Gel fraction w_g	Active chains n (mol/cm ³)
		<u>3% Diak #7</u>	
0.5	0.0252	0.451	2.0×10^{-7}
1	0.0486	0.654	1.3×10^{-6}
1.5	0.0659	0.771	3.3×10^{-6}
2	0.0826	0.798	6.3×10^{-6}
2.5	0.1275	0.818	2.1×10^{-5}
4.5	0.1246	0.881	2.0×10^{-5}
7.5	0.2432	0.999	3.5×10^{-4}
		<u>1.5% TMPTM</u>	
0.5	0.0646	0.656	2.9×10^{-6}
1	0.0702	0.710	3.8×10^{-6}
2	0.1114	0.807	1.4×10^{-5}
3	0.1210	0.828	1.8×10^{-5}
5	0.1351	0.851	2.5×10^{-5}
		<u>1.5% TMPTM/1.5% Diak #7</u>	
1	0.1697	0.893	4.9×10^{-5}
2	0.2041	0.927	8.6×10^{-5}
2.5	0.1673	0.901	4.7×10^{-5}
3	0.1843	0.911	6.3×10^{-5}
5	0.2280	0.931	1.2×10^{-4}
7.5	0.2397	0.933	1.3×10^{-4}
		<u>Untreated Viton GLT</u>	
0	dissolves	0	—

were essentially soluble.⁵ The preparations containing both monomers, 1.5% TMPTM/1.5% Diak #7, had a much lower amount of extractables (10%). The mixed-crosslinker system apparently uses the electron beam dose more efficiently to reduce the percent extractables and increase the crosslink density. The very low values of active chains found at low electron beam doses, of course, reflects a partly formed network which swells to 30–40 times its own volume in a good solvent. At higher beam doses a more stable network is formed.

Optical Properties

According to a modified form of the Beer–Lambert law

$$I = I_0 e^{-\tau x} \quad (7)$$

the intensity of the transmitted light I depends upon the incident intensity I_0 , the turbidity τ , and the path length x . Above 1% TMPTM, samples increased sharply in turbidity. The increase in turbidity with increasing concentration of TMPTM is thought to be a result of TMPTM homopolymerization, causing some phase separation.

The Diak #7 system does not show an increase in turbidity, an average of $\tau = 0.84$ being obtained independent of the Diak #7 concentration or radiation dose. In other words, the Diak #7 crosslinked materials remain reasonably clear.

The turbidity depends on the wavelength, however. When $\log \tau$ is plotted

vs. $\log \lambda$ (Fig. 5) a straight line is obtained, with a slope of -2.3 . Several other samples all gave straight lines with slopes in the -2.0 to -2.5 range. According to light-scattering theories^{15,16} this corresponds to a second phase of about 1000 \AA . Whether the turbidity, visible as a slight haze, is caused by residual soaps from the emulsion polymerization step, a slight blockiness in the structure with concomitant phase separation, or other causes is not yet known.

Stress-Strain Mechanical Studies

Stress-strain curves for Viton GLT samples were determined on an Instron tensile testing machine. Tensile strength, defined as the stress (per unit initial cross section) to break, increases TMPTM level, as shown in Figure 6.

Increasing the TMPTM concentration at 2.5 Mrad serves to greatly increase the tensile strength, whereas increasing the Diak #7 concentration at 2 Mrad does little to affect the tensile strength. With increasing concentration of crosslinking reagent, both crosslinkers serve to decrease the elongation to break.

The effect of increasing radiation dose, while holding the concentration of Diak #7 crosslinker constant, is shown in Table IV. With increasing dosage, tensile strength goes through a maximum at 2 Mrad. Percent elongation to break decreases as a function of increasing dose level.

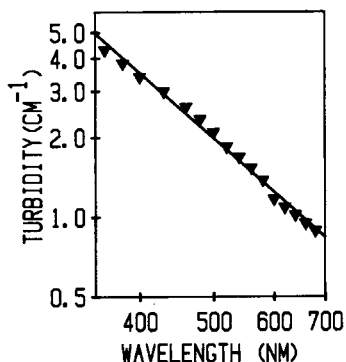


Fig. 5. Viton GLT (1.5% TMPTM/1.5% Diak #7/3 Mrad). The straight line obtained indicates a second phase of about 1000 \AA .

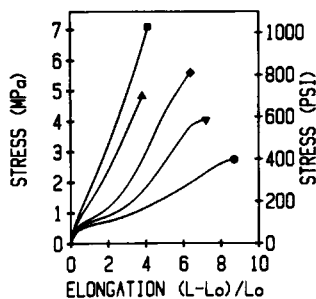


Fig. 6. Stress-strain behavior of Viton GLT at 2.5 Mrads: effect of TMPTM concentration. (●) 0%; (▼) 1%; (◆) 2%; (▲) 3%; (■) 5%.

TABLE IV
Stress-Strain Studies as a Function of Electron Beam Level (3% Diak #7)

Sample (Mrad)	Tensile strength (MPa)	% Elongation to break	Work to break (J/cm ³)	Young's modulus (MPa)	Active chains × 10 ⁻⁴ (mol/cm ³)
0.5	1.98	744	9.38	2.45	3.35
1.0	4.20	637	11.3	2.88	3.94
1.5	4.52	445	8.48	3.34	4.57
2.0	4.63	424	7.17	2.18	2.98
2.5	4.49	416	7.17	2.97	4.06
3.0	2.95	324	4.23	3.00	4.10
4.5	2.55	215	2.30	2.69	3.68
6.0	2.21	186	1.91	2.90	3.97
7.5	3.10	114	1.45	2.37	3.24

The effect of radiation upon the mixed crosslinker systems (1% TMPTM/1% Diak #7) and (2% TMPTM/2% Diak #7) is shown in Table V. Optimum properties are obtained at 1-3-Mrad irradiation.

DISCUSSION

Crosslinking and Degradation

The ratio of degradation to crosslinking of the Viton GLT/multifunctional monomer systems during irradiation can be determined graphically via the Charlesby-Pinner¹⁷ equation

$$S + S^{1/2} = (AP_n)^{-1}D^{-1} + B/A \quad (8)$$

when P_n is the initial average degree of polymerization, S is the sol fraction, D is the radiation dose in Mrad, A is the crosslinking coefficient, and b is the degradation coefficient. A plot of $S + S^{1/2}$ vs. D^{-1} gives the ratio of degradation

TABLE V
Stress-Strain Studies: Use of Mixed Crosslinkers

Sample (Mrad)	Tensile strength (MPa)	% Elongation to break	Work to break (J/cm ³)	Young's modulus (MPa)	Active chains × 10 ⁻⁴ (mol/cm ³)
<u>1% TMPTM/1% Diak #7</u>					
1.0	5.48	783	15.7	3.59	4.91
2.0	5.07	637	12.0	2.65	3.63
3.0	2.94	402	5.27	3.14	4.30
6.0	1.32	172	1.32	3.07	4.20
<u>2% TMPTM/2% Diak #7</u>					
0.5	5.22	399	9.45	4.15	5.68
1.0	4.44	308	6.32	2.71	3.71
2.0	5.41	285	6.60	2.61	3.57
3.0	5.47	239	5.18	3.11	4.26
4.5	5.41	234	5.11	2.56	3.50
6.0	3.45	183	2.60	2.14	2.93

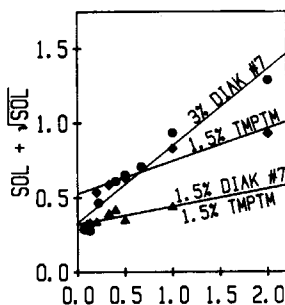


Fig. 7. Charlesby plot: intercept yields the degradation/crosslinking ratio. (●) 3% DIAK #7; (◆) 1.5% TMPTM; (▲) 1.5%/1.5%.

to crosslinking (B/A) directly from the intercept (Fig. 7). Also, eq. (8) was derived with the assumption of only polymer being present: i.e., the absence of a crosslinking monomer.

The TMPTM system appears more susceptible to degradation than the 3% Diak #7 system or the mixed system, 1.5% TMPTM/1.5% Diak #7 (see Table VI). The 3% Diak #7 system has a stronger dependence upon radiation dosage, as indicated by its greater slope in Figure 7 and Table VI. The gel point here is defined as the point where the sol fraction falls below unity. An extrapolation to the point where $S + S^{1/2}$ is equal to 2 yields the radiation dose level for incipient gelation (see Table VI).

The effect of radiation upon the crude material without multifunctional monomers is considered next. Viton GLT has mers with two different types of behavior towards radiation [eq. (1)]. The perfluoro(methyl vinyl ether) mer is of the type in which main chain scission predominates, because of the weakening steric strain of the alpha-substituent on the carbon bearing the side chain. The vinylidene fluoride mer is more capable of crosslinking because of its hydrogens.

The occurrence of crosslinking is attributed to the formation of polymer radicals at adjacent sites on neighboring chains which can arise from random events or from the initially ejected hydrogen removing a neighboring hydrogen atom, forming a hydrogen molecule.¹⁷

Effect of Multifunctional Monomers

The presence of multifunctional monomers enhances the crosslinking of Viton GLT. The monomers operate by either inhibiting chain scission, converting chain scission into a crosslinking reaction, or graft polymerization of the additive. There seems to be considerable argument over these possibilities in the literature.^{17,18} It is also possible that all three are in operation at the same time.

TABLE VI
Charlesby Parameters: Ratio of Degradation to Crosslinking, B/A , and Gel Point

System	Slope	B/A	Gel point (Mrad)
3% Diak #7	0.518	0.33	0.31
1.5% TMPTM	0.219	0.53	0.15
1.5% TMPTM/1.5% Diak #7	0.112	0.32	0.07

The differences in behavior between the two crosslinking monomers can be rationalized by looking at the structural differences between the two [structures (2) and (3)]. The double bonds of TMPTM are conjugated to ester groups, which activate the double bond. In Diak #7, this conjugation is absent. TMPTM polymerizes at lower temperatures than Diak #7. There is a possibility that TMPTM is homopolymerizing under molding conditions; this would lead to fewer possibilities of grafting onto the Viton GLT chain and lead to the observed phase separation.

It may be postulated that the mixed crosslinker system has a higher grafting efficiency because the allylic hydrogen of the Diak #7 acts as a chain transfer agent, reducing the molecular weight of the crosslinking monomer link, and encouraging grafting.

It may also be postulated that the mixed crosslinker system has a higher grafting efficiency because of the following interaction: (1) The TMPTM is the more reactive initially because of the ester group conjugation. (2) The growing end of the TMPTM homopolymer chain is a resonance-stabilized radical; which is unreactive toward C—H bonds, reacting only with unsaturated species. (It can add by opening Π -bonds, but it cannot abstract, breaking σ -bond. This latter appears the more likely.) (3) If the molecule attacked by a Diak #7 radical is Viton GLT, grafting is the expected result. Or, it may be the TMPTM homopolymer, yielding a lower grafting efficiency. Chain transfer to another monomer molecule is also possible.

Only radical reactions have been considered up to this point. In an electron beam, cations and cation radicals also form. The conjugation of the methacrylate double bond to its carbonyl group prevents the cationic polymerization of TMPTM; because the carbonyl is electron withdrawing, destabilizing adjacent positive charges. However, Diak #7 type double bonds are unconjugated, and hence capable of both free radical and cationic polymerization, representing another mode of enhancement for the mixed crosslinker system.

CONCLUSIONS

The synthesis of a transparent fluorocarbon elastomer with good low temperature properties, high transparency, and good tensile strength has been shown. Viton GLT elastomers follow the theories of rubber elasticity and the time temperature superposition principle. While this is to be expected, this finding indicates that a wide range of physical polymer science concepts can be brought to bear in optimizing any desired materials. While systems using Diak #7 or TMPTM alone have good properties, a mixed system of TMPTM and Diak #7 reagents shows a better crosslinking efficiency with the same electron beam dose.

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