

# Temperature-Dependence Modeling of Highly Crosslinked Polymer Networks

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**ABSTRACT:** The dependence on the temperature of the state of a highly crosslinked polymer network can be modeled as a function of well-defined molecular-level network parameters to yield a simple applied model equation. The tightness and strength (modulus of elasticity) of the crosslinked networks formed, as well as any further tightening of the network due to further curing, can easily be compared with the parameters  $A$ ,  $M$ , and  $\alpha$  (the coefficient of branching) and the  $m/E$  ratio and, therefore, with parameters directly related to molecular-level characteristics of the system. The crosslinking contribution to the network is represented by  $A$  and  $M$ , the former representing the frequency of crosslinking and the latter having the dimensions of an

energy. The ratio  $m/E$ , that is, the ratio of the average number of degrees of freedom of chain segments between crosslinking nodes ( $m$ ) to the average energy of nonbonded atom interactions between the same segments ( $E$ ), and  $\alpha$  model the noncrosslinked contribution to the characteristics of the network. These are the same parameters that appear in the simple equation modeling the dependence of the characteristics of the network on the temperature within a limited temperature range. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2416–2426, 2003

**Key words:** networks; modeling; crosslinking; density; transitions

## INTRODUCTION

Crosslinked polymers can display significant viscoelastic responses over large temperature ranges and timescales.<sup>1–4</sup> Although rigorous molecular models exist for uncrosslinked polymers,<sup>5,6</sup> molecular-level mechanisms for the viscoelasticity of fully crosslinked polymers have also been proposed more recently, and models for rationalizing the effects of time and temperature on the viscoelastic behavior of polymers have been constructed and presented.<sup>7</sup>

The measurement of polymer dynamic properties typically employs either isothermal frequency sweeps or isochronal temperature sweeps. Although time-temperature superpositioning (TTS) has been used successfully to overcome the isotherm shortcoming of not being able to capture all of a material's viscoelastic behavior in a single experiment because of practical limits in the deformation frequency, both the accuracy and validity of TTS have been questioned.<sup>8</sup>

It has recently been shown that thermomechanical analysis (TMA) at a constant heating rate is a technique that lends itself well to the interpretation of the viscoelastic properties of polymers. Therefore, work on the formation of polymer networks by photopoly-

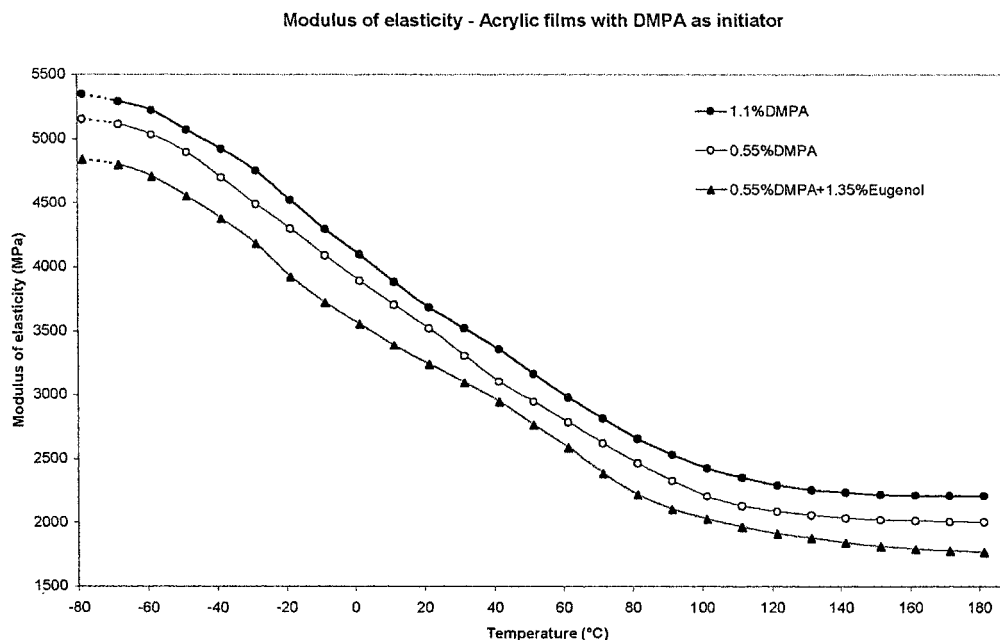
merizable and polyester surface finishes, as well as polycondensation resins on wood, has yielded a mathematical relationship<sup>9–14</sup> for the energy of interaction ( $E$ ) at the resin/substrate interface calculated by molecular mechanics (work of adhesion), the number of degrees of freedom ( $m$ ) of the segment of the synthetic polymer between two crosslinking nodes, the coefficient of branching ( $\alpha$ ) and, therefore, the functionality of the starting monomer, and the relative deflection ( $f$ ) obtained by TMA of wood specimens coated with the resin through the expression  $f = -km/\alpha E$ , where  $k$  is a constant.<sup>9–14</sup> These results were obtained on crosslinked polymers of a different nature and of a different extent of crosslinking but still supported by a well-defined substrate aimed at the study of interfacial adhesion.<sup>9–14</sup> The same technique however, opens a definite possibility for the determination of the viscoelastic characteristics of the same polymers, although not supported by a substrate, and for the definition of equations similar to that previously mentioned.

This article deals with the study of the viscoelastic characteristics of the same polymers, unsupported by a substrate, followed by TMA.

## EXPERIMENTAL

Trimethylolpropane triacrylate (TMPTA)<sup>9</sup> was hardened by the addition of two radical initiators, 2,2-dimethoxy-2-phenylacetophenone (DMPA) or an

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**Figure 1** Variation of MOE as a function of temperature for acrylic films of (●) TMPTA and 1.1% DMPA, (○) TMPTA and 0.55% DMPA, and (▲) TMPTA, 0.55% DMPA, and 1.35% eugenol.

equimolar mix of benzophenone and methyl diethanolamine (MDEA) in the presence or absence of inhibitors. The inhibitors used were phenol, eugenol (2-methoxy-4-propenyl phenol), and 2,6-dimethoxyphenol (DMP) in molar proportions, as indicated in the tables. The test specimens were prepared by the resin and additive mix being poured into a Teflon mold with removable side walls. The specimens were cured by UV irradiation. The cured specimens were cut to 21 mm × 6 mm, and their thickness was sanded down to 0.6 mm, first with 180-mesh sandpaper and then with 400-mesh sandpaper.

The modulus of elasticity (MOE) of the cured specimens was measured isothermally with a Mettler TMA 40 thermomechanical analyzer (Zurich, Switzerland) at 20°C intervals starting at 25°C and ending at 185°C. For isothermal measurements by TMA, the samples needed to be conditioned to thermal equilibrium, and a certain time was needed to reach this equilibrium. This time was optimized to 6 min for all the test temperatures, except for 25°C (1 min). In all cases, only the data of the last 60 s were used to calculate MOE. The MOE measured values reported were all averages of five samples. MOE was calculated by the TMA deflection ( $\Delta f$ ) with the classical mechanics relationship:  $MOE = [L^3 / (4bh^3)] [\Delta F / (\Delta f)]$ .

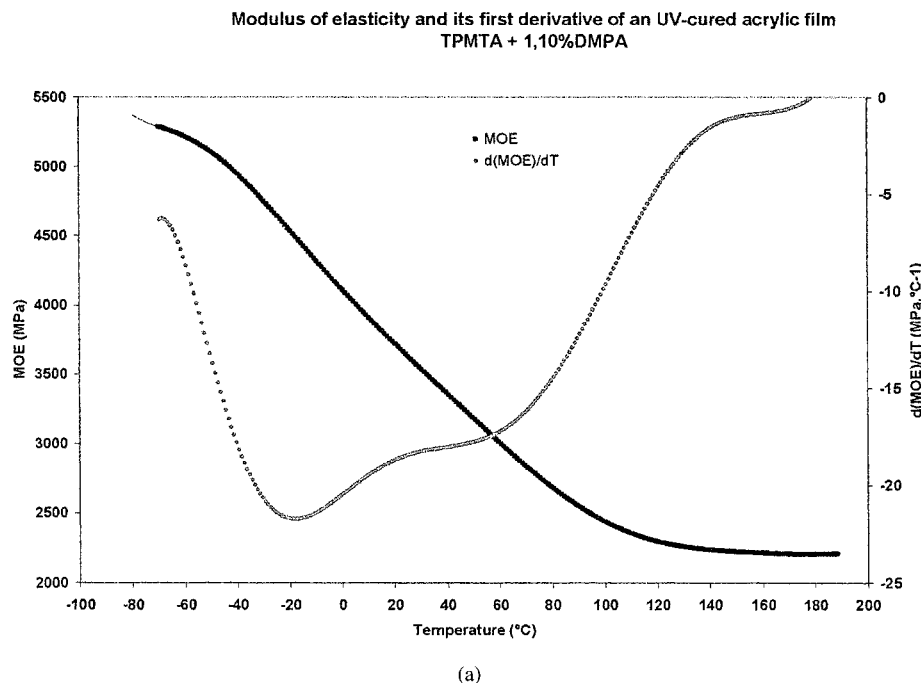
Tests were also carried out with the same types of specimens and the same type of TMA equipment, but this time with a cooler in the temperature range of -80 to 190°C. The measurements, however, were not isothermal but were carried out at a constant heating rate of 5°C/min. A 15-min thermal stabilization time was given

to the samples at -80°C, and at each temperature, the MOE value obtained was the average of 10 specimens.

## DISCUSSION

In Figure 1 are shown the curves of the variation of MOE as a function of temperature at a constant heating rate for pure, unsupported crosslinked acrylic films cured with two different levels of DMPA as an initiator and, in one case, with the addition of a phenol (eugenol) as an additive interfering with the radical mechanism of the curing of the acrylic polymer. There can be seen in this figure the presence of the glassy-state plateau in the -80 to -60°C range, the viscoelastic transition zone in the -60 to +120°C range, and the stabilization of the curve to the rubbery-state plateau at temperatures higher than 120°C. The three cases appear to have very similar glass-transition temperatures in the -56 to -58°C range, with a higher level of crosslinking presenting a curve shifted at higher modulus values. This is followed by a less crosslinked material because of the lower initiator percentage, with the lowest MOE curve belonging to a material in which the crosslinking density is further decreased by the addition of a phenolic inhibitor. However, the curves in Figure 1 indicate that the decrease in the modulus is not uniform, as can be shown by the drawing of the first derivatives of the MOE curves.

To obtain a smooth curve of the first derivative, we first performed a polynomial curve fit of the modulus curves, and we calculated the derivative with the fitted MOE data values. Comparing the fitted values and



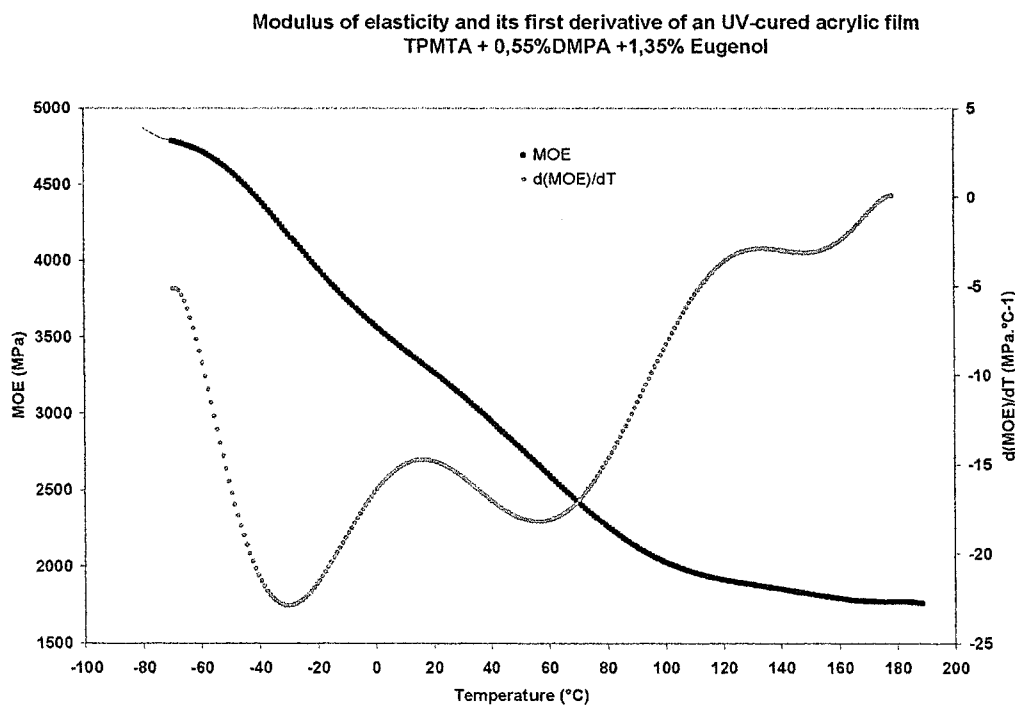
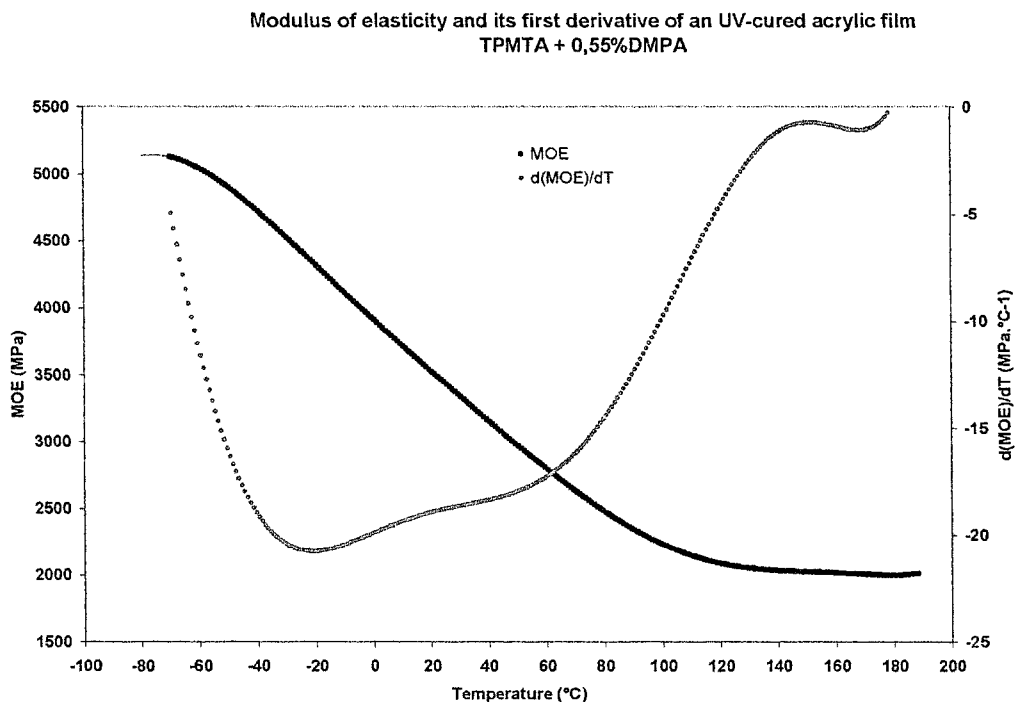
**Figure 2** Curve of the variation of MOE as a function of temperature and its first derivative for acrylic films of (a) TPMTA and 1.1% DMPA, (b) TPMTA and 0.55% DMPA, and (c) TPMTA, 0.55% DMPA, and 1.35% eugenol.

the original data, we found that the maximum errors in the modulus introduced by the polynomial fit at all temperatures was less than 1.5% in all cases and that the coefficient of correlation ( $r^2$ ) was greater than 0.999. Consequently, the polynomial fit does not change the appearance of the MOE curve, but the resultant derivative curve is a smooth one. The direct smoothing of the derivative curve would introduce more significant errors. The derivative curves in Figure 2(a–c) show that MOE decreases rapidly from  $-70^\circ\text{C}$  down to  $-20^\circ\text{C}$  for all three films. At temperatures higher than  $-20^\circ\text{C}$ , the decrease in MOE depends on the formulation of the film. Without the addition of eugenol, the first derivative decreases with increasing temperature, with the appearance of a shoulder between  $-20$  and  $60^\circ\text{C}$ ; this indicates that a low-intensity secondary transition, due to a structural characteristic of the acrylic film itself, occurs in this temperature interval. With the addition of eugenol, this shoulder transforms itself into a definite, separate peak at  $+15^\circ\text{C}$ , which might indicate that the presence of eugenol has altered the structure of the cured film and noticeably increased the extent and intensity of the secondary transition. It is difficult with the data available to decide what this secondary transition is. It is (1) likely due to an increase in pendant side chains or chain terminations, (2) even more likely due to an increase in the mobility of the chain segments between crosslinking nodes on account of their increase in average length, or (3) most likely due to both. This is due to the lower average crosslinking density of the net-

work from the interference in the radical crosslinking mechanism induced by the presence of the phenolic moieties of eugenol in case 2 and by the termination of chains induced by the coreaction with the acrylic polymer of the unsaturated side chain of eugenol in case 1.

In Figures 3 and 4 are shown trends similar to those shown previously when the initiator is changed to a different type, namely, benzophenone/MDEA. However, the curves of MOE as a function of temperature in Figure 3 are less regular, and the decrease of MOE is much less uniform than in Figure 1. The temperatures at which MOE tends to level off are lower than those of the films with DMPA as an initiator, especially in the case including eugenol. This is an indication that the level of crosslinking of the same acrylic network is much lower when these initiators are used than when DMPA is used.

The same experiments were repeated with a polycondensation phenol–resorcinol–formaldehyde resin notorious for giving very tight, high-strength networks with very high crosslink density. The results are shown in Figure 5; again, the derivative peaks appear, but at lower temperatures than those of the cases discussed previously. However, the intensity of the first peak is lower for this very rigid resin, indicating that in this case we are indeed in the presence of a tighter, stronger network; both the temperature and the intensity of the first derivative peak are indeed important in determining what mobility (for any causes, chain terminals or longer internodal segments)

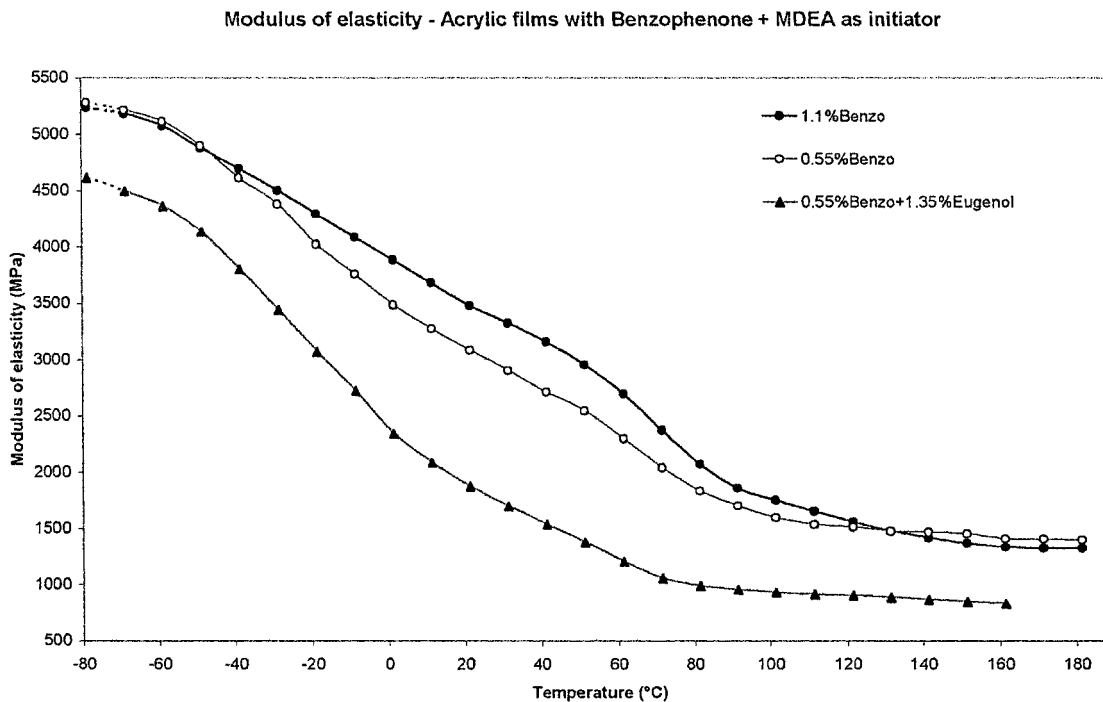


**Figure 2** (Continued from the previous page)

is induced in the finished network and how well crosslinked the network is.

Plots of  $\ln \text{MOE}$  versus  $1/RT$  (where  $R$  = perfect gas constant and  $T$  = temperature in degrees Kelvin (K)) have also been drawn (not shown) to determine if

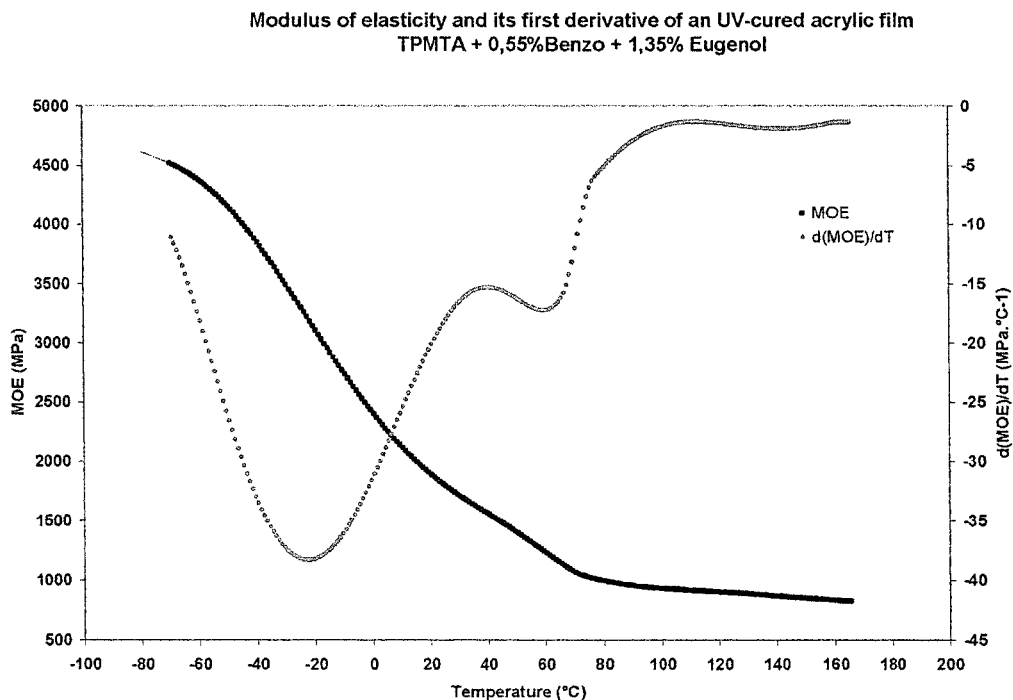
there is a linear relationship between temperature and MOE and if a constant activation energy can be obtained. A well-defined linear relationship could not be obtained for the whole range of temperatures; instead, the plots showed sigmoidal curves, indicating that it is



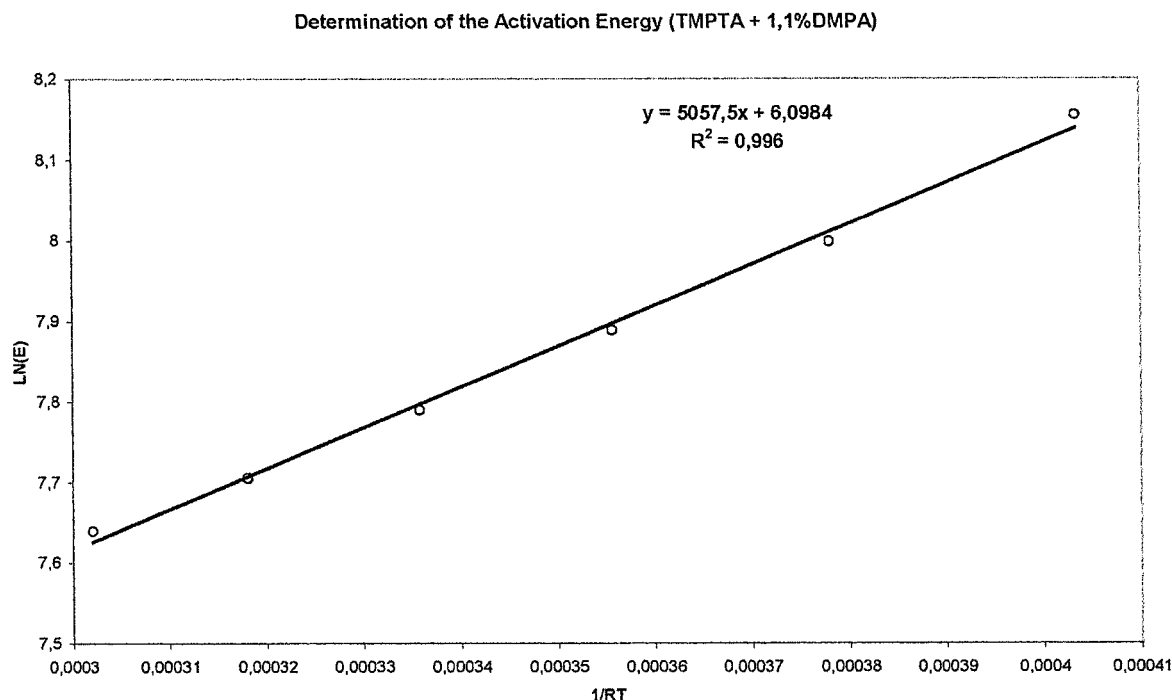
**Figure 3** Variation of MOE as a function of temperature for acrylic films of (●) TMPTA and 1.1% benzophenone/MDEA, (○) TMPTA and 0.55% benzophenone/MDEA, and (▲) TMPTA, 0.55% benzophenone/MDEA, and 1.35% eugenol.

not reasonable perhaps to attempt to establish a linear relationship between the two parameters over such a wide range of temperatures (from  $-80$  to  $+190^{\circ}\text{C}$ ).

However, linear plots of  $\ln$  MOE as a function of  $1/RT$  can be obtained with an excellent coefficient of correlation ( $r$ ) in a narrower but still rather wide tem-



**Figure 4** Curve of the variation of MOE as a function of temperature and its first derivative for acrylic films of TPMTA, 0.55% benzophenone/MDEA, and 1.35% eugenol.



**Figure 5** Linear regression fit for  $\ln$  MOE as a function of  $1/RT$  for the determination of parameters  $A$  and  $M$  of acrylic films of TMPTA and 1.1% DMPA.

perature range. This was done in the 25–125°C temperature range. One of these linear plots is shown as an example in Figure 5. The value of  $f$  corresponding to 25°C, obtained from the value of MOE once MOE has stabilized and is not increasing anymore (this implies that full crosslinking has occurred), shown in Figure 5 for TMPTA/1.1% DMPA as an initiator, is 126.7  $\mu\text{m}$ .

From the equation  $f = -km/\alpha E$ , by considering that the maximum crosslinking possible has been obtained, and by introducing the theoretical values for the complete crosslinking of TMPTA<sup>9</sup> of  $m = 11$  and  $\alpha = 0.2$  and the already reported<sup>9</sup> value of  $E = -4.46$  kcal/mol (calculated by molecular mechanics), where  $E$  is the average energy of the interaction of segments between crosslinking nodes exclusively among non-bonded segments of the same polymer, one obtains a value of  $k = 10.274$  for the pure polymer,  $k = 42.99$  when  $E$  is instead expressed in kilojoules per mole, and  $k = 42,989$  when  $E$  is expressed in joules per mole. If this is extended to the cases in which half the amount of the DMPA initiator and half of the DMPA and interfering phenol eugenol have been added (Figs. 2 and 3), the values of  $m$  are 11.7 and 12.7, respectively. It has been assumed that crosslinking is complete in the 1.1% DMPA catalyzed case once MOE does not increase anymore, but this does not mean that the ultimate possible level of crosslinking of the system has been attained. Therefore, the given values of  $m$  are just relative, and all that can really be said is that for the other two cases, the average number of degrees of

freedom of the polymer segments between crosslinking nodes and, therefore, their length and molar mass in the other two networks increases 6.4 and 15.5%, respectively, over that of the 1.1% DMPA catalyzed case. This shows that the system does detect the loss of crosslinking density due to the lower initiator or the addition of an interfering additive and the relative trend of this decrease in the crosslinking density.

Equally, the straight regression line correlating  $\ln$  MOE and  $1/RT$  and the good correlation coefficients obtained [see Fig. 5 and Table III (shown later)] indicate that the variation of MOE and, by inference, the variation of  $1/f$  as a function of temperature can be described by an Arrhenius-type equation:

$$\text{MOE} = Ae^{M/RT} \quad (1)$$

or equally

$$\ln \text{MOE} = \ln A - \frac{M}{RT} \quad (2)$$

where for the first three cases in Table III (shown later),  $\ln A$  is 6.0984, 6.0905, and 6.0177 and  $M$ , obtained graphically from the figure slopes, is 5075.5, 4791.9, and 4931.4. Although the correlation is very clear, it is rather difficult to decide to what physical parameters  $A$  and  $M$  correspond. Because the expression refers to the dependence of the relative level of crosslinking of the network on the temperature, the

pre-exponential factor  $A$  appears to be a parameter referring to the frequency of crosslinking and, therefore, to the density of the crosslinking of the network. As such, the value of  $\ln A$  progressively decreases, passing from the 1.1% DMPA catalyzed case to the less catalyzed case and to the case less catalyzed and having an interfering agent, supporting such an hypothesis. However, this parameter could describe network crosslinking density/frequency either per unit volume or per unit of polymer mass. As the polymer will expand with temperature, the parameter is more likely to describe network crosslinking density per unit of polymer mass. Its dimensions are  $\text{N}/\text{m}^2$ , as for MOE. It is considerably more difficult to imagine what parameter  $M$  describes. As the higher  $M$  is, the higher is the value of the network MOE, and as  $M$  has the dimensions of an energy, only three approximations can be used to identify  $M$  as: (1) the energy inherent to the hardened network contributed by crosslinking; (2) the energy inherent to the hardened network contributed by all the segments between the network nodes, but in this case all the nodes, thus both the crosslinking and entanglement ones, describing both crosslinking and entanglement contributions to the network strength/cohesion, or (3) the energy needed to activate crosslinking in the network, although this latter possibility appears to be rather unlikely. It is not possible with just the data available to decide which of these possibilities is the most likely.

If eq. (2) is coupled with eq. (3)

$$\Delta f = -\frac{km}{\alpha E} \quad (3)$$

and if we consider the relationship of MOE and  $\Delta f$  described by expression (4)

$$\text{MOE} = [L^3/(4bh^3)][\Delta F/(\Delta f)] \quad (4)$$

and make it equal to  $B = [L^3/(4bh^3)]$  to facilitate calculations, we find that

$$\Delta f = \frac{B\Delta F}{Ae^{M/RT}} \quad (5)$$

This correlates the deflection obtained experimentally by TMA with the temperature and degree of crosslinking and entanglement (if any) of the sample. Equally, from eqs. (3) and (5), eq. (6) can be obtained:

$$-\frac{km}{\alpha E} = \frac{B\Delta F}{Ae^{M/RT}} \quad (6)$$

where  $k$  is a constant depending on the testing conditions used and  $B$  is a constant depending on the dimensions of the sample. In the experiments carried

out,  $\Delta F$  was also kept constant at 0.4 N. Equation (6) correlates  $m$  for network chain segments between crosslinking nodes of a hardened network.  $E$  is defined as the average energy of the interaction of segments between crosslinking nodes exclusively among nonbonded segments of the same polymer; as such,  $E$  is the average of the energy of nonlinked atom interactions of the network and, therefore, of the internal cohesive energy of the synthetic polymer due to secondary forces, other than that contributed by crosslinking.  $T$  is the temperature at which the network finds itself, the density of its crosslinking, and the contribution of crosslinking being described by the frequency of the crosslinking parameter  $A$ , the parameter  $M$ , and  $\alpha$ . It is clear by their definitions that  $m$ ,  $M$ ,  $A$ , and  $\alpha$  are all related and describe different contributions to the same physical state in which the network finds itself. By simplifying eq. (6) by combining in a single constant what is kept constant in the experiments carried out [ $k' = (B\Delta F)/k$ ], we obtain

$$\frac{m}{E} = -k' \frac{\alpha}{Ae^{M/RT}} \quad (7)$$

This equation indicates logically that the lower  $\alpha$  is (by definition,  $\alpha$  is lower the higher the functionality is and, therefore, the higher the branching is<sup>9,15</sup>), the lower  $m$  is, and that the lower  $m$  is, the lower  $E$  is. Therefore,  $m$ ,  $\alpha$ , and  $E$  describe the state of the hardened network, not including the contribution given by crosslinking itself. Equally logically, as  $m$  for segments between crosslinking nodes decreases as the network becomes more crosslinked, the density/frequency of crosslinking parameter  $A$  should also increase, as indeed is the case and is indicated by eq. (7) and Table I. This indicates that although it appears to be the one strictly defined by the parameters  $A$  and  $M$ , although for  $M$  this is not sure, the hardened polymer network behaves as a single entity defined by all five parameters ( $m$ ,  $\alpha$ ,  $E$ ,  $A$ , and  $M$ ). However, eq. (7) also correlates the temperature of the system with all these parameters that define the network at the molecular level. Notwithstanding that such an equation is only shown here to be valid in the relatively limited temperature range of 25–125°C, in which a linear relationship between MOE and  $1/T$  was obtained for the systems studied, it does nonetheless constitute a simple experimental model showing the influence of the temperature on the parameters defining the polymer network.

For TMPTA and 1.1% DMPA, with which complete crosslinking occurs, Table I indicates the value of  $E$ , which is known,<sup>9</sup> and the corresponding value of  $m$ . The values of the  $m/E$  ratio and  $E$  can be calculated (Table II) because  $m$  always remains the same, here

**TABLE I**  
Parameter Values Used in Eq. (7) for the TMPTA Cases Catalyzed by DMPA

Parameter	1.1% DMPA	0.55% DMPA	0.55% DMPA and eugenol
<i>A</i>	445.15	441.64	410.63
<i>M</i>	5075.5	4791.9	4931.4
<i>R</i> (J/mol K)	← 8.315 →		
<i>m</i>	11		
$\alpha$	0.2	0.2	0.2
<i>E</i> (J/mol)	-18661		
<i>k</i>	42989	42989	42989
<i>B</i>	$L = 18 \text{ mm} = 0.018 \text{ m}$ $b = 6 \text{ mm} = 0.006 \text{ m}$ $h = 0.6 \text{ mm} = 0.0006 \text{ m}$ $B = 5.83 \times 10^{-6} / (4 \times 0.006 \times 2.16 \times 10^{-10}) =$		
$\Delta F$ (N)	0.4	0.4	0.4
$k' = B\Delta F/k = (1,124,614.198 \times 0.4)/41,460 =$	← 10.4642 →		

being equal to 11. Where complete, maximum crosslinking is not achieved, as for cases 2 and 3, both *m* and *E* are not known and vary (*m* decreases because of the lower average level of crosslinking, and *E* increases because of the longer average length of segments between crosslinking nodes), and as a result, the only sure parameter that can be used for comparison is the *m/E* ratio (Table II).

The first result evident from Table II is that the *m/E* ratio increases with increasing temperature. As *m* remains by definition the same as the temperature varies when the chain segment between nodes is relatively short (which is always the case here), the variation of the *m/E* ratio as the temperature increases is due to the decrease of *E*. This is expected because as the temperature increases, so does the empty volume;

**TABLE II**  
Results for the *m/E* Ratio Obtained for Different Cases with Eq. (7) and the Experimental Values of Parameters *A* and *M* and a Comparison with MOE Values

<i>T</i>		<i>m/E</i> ( $\times 10^{-3}$ )	<i>E</i> <sup>a</sup> (kJ/mol)	<i>E</i> <sup>a</sup>	<i>m</i> <sup>a</sup>	MOE experimental (MPa)
(°C)	<i>K</i>					
TMPTA and 1.1% DMPA						
	21	0.590	18.64		11	—
	25	0.606	18.15			3550
	45	0.690	15.94			2997
	65	0.772	14.25			2660
	85	0.854	12.88			2414
	105	0.935	11.76			2233
	125	1.014	10.84			2119
TMPTA and 0.55% DMPA						
	25	0.685	16.06	17.81	12.2	3186
	45	0.774	14.21	15.76		2674
	65	0.861	12.78	14.17		2396
	85	0.947	11.62	12.88		2184
	105	1.032	10.66	11.82		2039
	125	1.114	9.87	10.95		1962
TMPTA, 0.55% DMPA, and 1.35% eugenol						
	25	0.697	15.78	18.44	12.9	3038
	45	0.789	13.94	16.29		2593
	65	0.882	12.47	14.57		2299
	85	0.972	11.31	13.22		2095
	105	1.061	10.37	12.11		1964
	125	1.149	9.57	11.18		1859

<sup>a</sup> With the assumption of *m* fixed at the given value of 11. For cases 2 and 3, the value of *E* would be overestimated as one should assume that *m* = 11 (first *E* column), and this is not the case in a less tight network. Thus, we calculated in the second *E* column from the MOE  $m = 3186/3550 \times 11 = 12.2$  as a linear approximation and recalculated the *E* starting from this value of *m* from the *m/E* ratio obtained experimentally from eq. (7): this is the value reported for case 2 in the table, in the second *E* column. The same was done for case 3.



TABLE III  
Values of Parameters  $A$  and  $M$  for Different TMPTA Networks for Linear Plots of  $\ln$  MOE as a Function of  $1/RT$  with Their Relative Temperature Intervals

Initiator type	Molar proportion (%)	Inhibitor type	Molar proportion (%)	$M$	$\ln A$	$r^2$	Temperature range (°C)
DMPA	1.10	—	—	5057.5	6.0984	0.996	20–125
DMPA	0.55	—	—	4791.9	6.0905	0.990	25–125
DMPA	0.55	Eugenol	1.35	4931.4	6.0177	0.995	25–125
DMPA	0.55	DMP	1.35	5286.3	5.8792	0.995	25–125
DMPA	0.55	Phenol	1.35	5355.8	5.8265	0.995	25–125
Benzophenone/MDEA	1.10	—	—	7468.2	4.9302	0.999	25–125
Benzophenone/MDEA	0.55	—	—	6128.8	5.3362	0.995	25–125
Benzophenone/MDEA	0.55	Eugenol	1.35	4737.8	5.4000	0.920	25–125
Benzophenone/MDEA	0.55	Eugenol	1.35	7855.1	4.3416	0.941	65–125
Benzophenone/MDEA	0.55	Eugenol	1.35	2050.8	6.4433	0.980	25–65
Benzophenone/MDEA	0.55	DMP	1.35	4258.7	5.5504	0.923	25–125
Benzophenone/MDEA	0.55	DMP	1.35	6826.3	4.7373	0.994	85–125
Benzophenone/MDEA	0.55	DMP	1.35	1707.9	6.5572	0.924	25–85
Benzophenone/MDEA	0.55	Phenol	1.35	6344.3	5.0127	0.977	25–125

therefore, the average dynamic distance between segments increases with a consequent decrease in the nonbonded chain/chain secondary force interactions. This trend is valid for all cases, whatever the relative tightness of the network (but always in very crosslinked networks in which the entanglement of chain segments between crosslinking nodes is minimal or does not occur). The second trend of importance, corresponding to what is expected, is that as the temperature increases, the  $m/E$  ratio is higher at each temperature considered as one passes to less crosslinked networks (Table II). This is due mainly to the value of  $m$  being higher than expected in a less tight network. This would be a means to calculate  $m$  rather exactly if one did not expect the value of  $E$  to increase as well; which should be the case for a higher level of interchain secondary force interactions due to the longer average length of segments between crosslinking nodes.

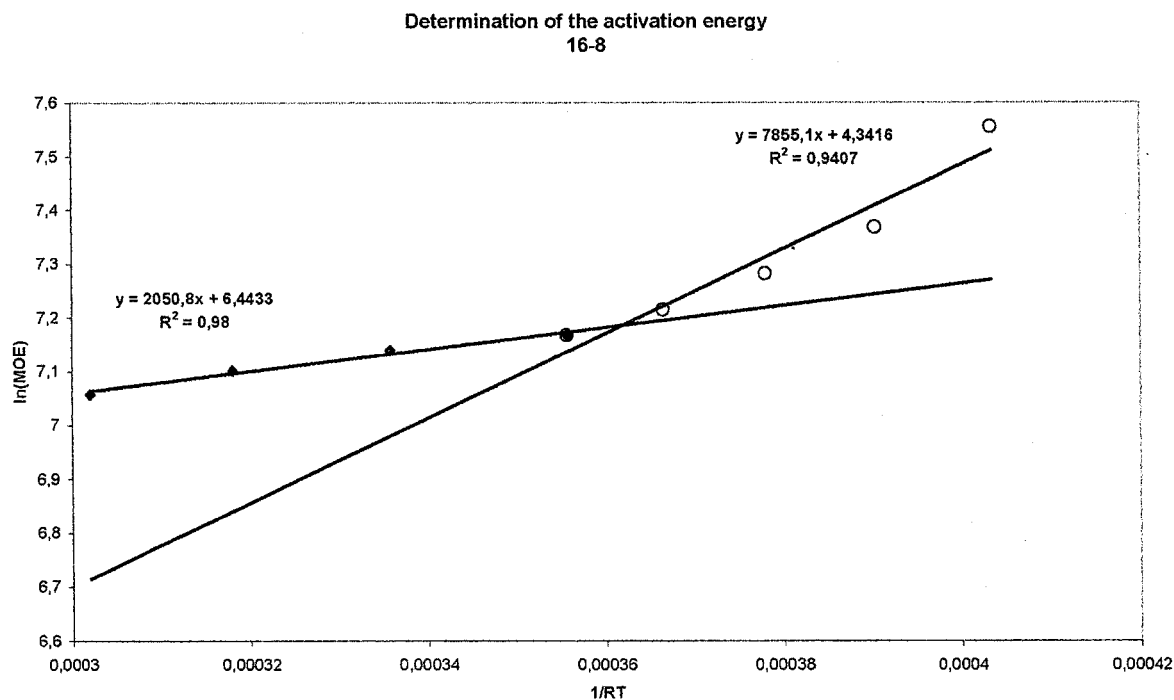
Table II has two columns presenting different values of  $E$  for the cases with half of the DMPA initiator

and with half of the DMPA initiator and eugenol as an added inhibitor. The problem is that, although in the first case (1.1% DMPA)  $m$  is known and  $E$  is also known at 21°C, this is not true for the other two cases. Therefore, in the other two cases,  $m$  is greater as lower crosslinking is obtained and  $E$  is correspondingly larger too, but it cannot and has not been calculated by theoretical means.<sup>9</sup> This means that for cases 2 and 3 in Table II, the value of  $E$  would be overestimated if it is assumed that  $m$  is equal to 11 (first  $E$  column), but this is not the case in a less tight network. Therefore, if one approximates from MOE of case 2 with respect to case 1, the second  $E$  column can be calculated from the MOE ratio with  $m = 3186/3550 \times 11 = 12.2$  as a linear approximation.  $E$  is recalculated from this value of  $m$  from the  $m/E$  ratio obtained experimentally from eq. (7): this is the value reported for case 2 in the second  $E$  column. The same was done for case 3 in Table III.

To determine if eq. (7) might have wider applicability, we looked for and found linear relationships between  $\ln$  MOE and  $1/RT$  for several other network

TABLE IV  
Experimental MOE Values at Different Temperatures of TMPTA-Hardened Networks

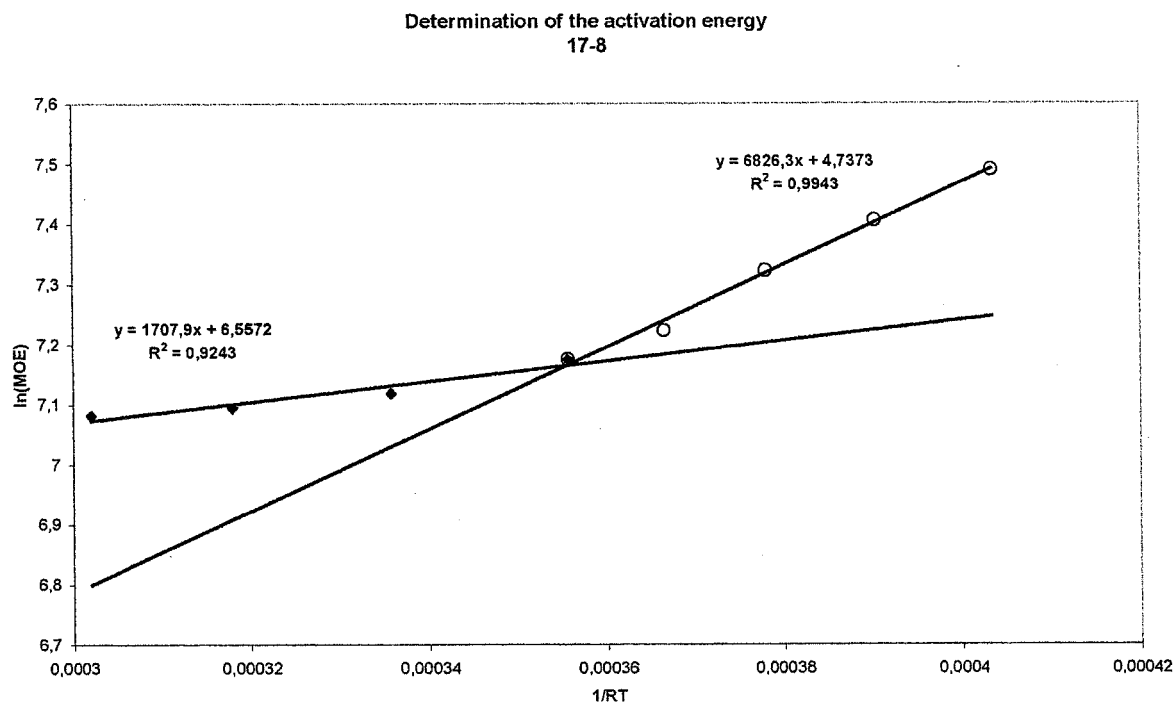
Initiator type	Molar proportion (%)	Inhibitor type	Molar proportion (%)	MOE (MPa)					
				25°C	45°C	65°C	85°C	105°C	125°C
DMPA	1.10	—	—	3550	2997	2660	2414	2233	2119
DMPA	0.55	—	—	3186	2674	2396	2184	2039	1962
DMPA	0.55	Eugenol	1.35	3038	2593	2299	2095	1964	1859
DMPA	0.55	DMP	1.35	3057	2557	2262	2058	1907	1805
DMPA	0.55	Phenol	1.35	3066	2569	2258	2039	1877	1783
Benzophenone/MDEA	1.10	—	—	2813	2273	1939	1678	1457	1328
Benzophenone/MDEA	0.55	—	—	2487	2061	1784	1576	1438	1367
Benzophenone/MDEA	0.55	Eugenol	1.35	1564	1238	1109	1055	1018	981
Benzophenone/MDEA	0.55	DMP	1.35	1704	1359	1217	1161	1124	1087
Benzophenone/MDEA	0.55	Phenol	1.35	2046	1598	1365	1228	1145	1091



**Figure 6** First of two examples of the discontinuity of properties due to the restart of curing of an incompletely cured network in the linear regression fit for ln MOE as a function of 1/RT for the determination of parameters A and M of acrylic films of TMPTA, 0.55% benzophenone/MDEA, and 1.35% eugenol.

types. Therefore, a network formed with the same acrylic monomer (TMPTA), but with a different initiator (an equimolar mix of benzophenone and MDEA),

was studied at two levels of the initiator (1.1 and 0.55%) and with the addition of the same three phenolic inhibitors used previously. The values of the



**Figure 7** Second of two examples of the discontinuity of properties due to the restart of curing of an incompletely cured network in the linear regression fit for ln MOE as a function of 1/RT for the determination of parameters A and M of acrylic films of TMPTA, 0.55% benzophenone/MDEA, and 1.35% DMP.

TABLE V  
Results for the Discontinuity in the  $m/E$  Ratio Obtained with Eq. (7) for Cases in Which Further Network Curing and Tightening Restarted once a Higher Temperature was Reached

	$m/E (\times 10^{-3})$					
	298 K	318 K	338 K	358 K	378 K	398 K
½Benzophenone/MDEA, 25–125°C, Control	0.85	0.99	1.14	1.29	1.43	1.58
½Benzophenone/MDEA + eugenol, 25–65°C	1.15	1.40	1.67			
½Benzophenone/MDEA + eugenol, 65–125°C				1.67	1.73	1.78
½Benzophenone/MDEA + DMP, 25–85°C	1.17	1.39	1.62	1.85		
½Benzophenone/MDEA + DMP, 85–125°C				1.67	1.73	1.77

parameters  $M$  and  $\ln A$  from eq. (2) and of  $r^2$ , which were obtained in the linear regression analysis of  $\ln$  MOE and  $1/RT$ , are shown in Table III. They indicate that the tightness of the networks formed with the alternate initiator is lower and that the networks are less crosslinked than in the DMPA-initiated cases; this result is supported by the MOE values for all the systems reported in Table IV. They are compared to the values of the same parameters obtained for the cases already discussed. The correlations obtained are good and indicate that at least within the limits of the type of acrylic networks at hand, eq. (7) appears to be widely applicable. It also indicates that the tightness and strength (MOE) of the networks formed can easily be compared with the parameters  $A$ ,  $M$ , and  $\alpha$  and the  $m/E$  ratio and, therefore, with parameters directly related to molecular-level characteristics of the system. Even in cases in which more complex physical effects do occur, eq. (7) appears to indicate more clearly the characteristics of the network. Therefore, in the cases catalyzed by the equimolar benzophenone/MDEA mix, in which eugenol and DMP are used as inhibitors, the coefficient of correlation is low, as the figure clearly indicates a discontinuity of properties (only the cases in Figs. 6 and 7). The two parts can then be modeled separately. In the cases at hand (Tables III and V and Figs. 6 and 7), a comparison of the  $m/E$  ratio indicates that the network level of crosslinking is relatively low. As the temperature increases, a temperature is reached at which curing and tightening of the network (not completely or sufficiently cured) start again, and the further curing causes the  $m/E$  ratio of the system to converge toward the value of the case in which no inhibitor is added. In the case in which the inhibitor used is DMP, the network contraction due to the starting of further curing at 85°C is particularly evident from the  $m/E$  discontinuity at this temperature in Table V and in both cases in Figures 6 and 7. This indicates too that eq. (7), which has been used to calculate the  $m/E$  ratio from the experimentally determined values of  $A$  and  $M$ , does indeed describe well the total adhesive system, namely, both the existing crosslinking and the competing effects induced by the

temperature on the network. These competing effects are (1) the increase in the segmental mobility due to the empty volume increase with the increase in the temperature and (2) any further tightening of the network due to further curing.

## CONCLUSIONS

The dependence on the temperature of the state of a highly crosslinked polymer network can be modeled as a function of well-defined molecular-level network parameters to yield a simple applied model equation. The tightness and strength (MOE) of the crosslinked networks formed, as well as any further tightening of the network due to further curing, can easily be compared with the parameters  $A$ ,  $M$ , and  $\alpha$  and the  $m/E$  ratio and, therefore, with parameters directly related to molecular-level characteristics of the system. These are the same parameters that appear in the simple equation modeling the dependence of the characteristic of the network on the temperature within a limited temperature range.

## References

- Miyase, A.; Chen, A. W.-L.; Geil, P. H.; Wang, S. S. *J Compos Mater* 1993, 27, 886.
- Miyase, A.; Wang, S. S.; Chen, A. W.-L.; Geil, P. H. *J Compos Mater* 1993, 27, 908.
- Crossman, F. W.; Mauri, R. E.; Warren, W. J. In *Advanced Composite Materials—Environment Effects*; ASTM STP 658; Vinson, J. R., Ed.; American Society for Testing and Materials: Philadelphia, 1978; p 205.
- Brinson, L. C.; Knauss, W. G. *J Mech Phys Solids* 1991, 39, 859.
- Rouse, P. E. *J Chem Phys* 1953, 21, 1272.
- Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
- Simon, P. P.; Ploehn, H. J. *J Rheol* 1997, 41, 641.
- Plazek, D. J. *J Polym Sci Part A-2: Polym Phys* 1968, 6, 621.
- Pizzi, A.; Probst, F.; Deglise, X. *J Adhes Sci Technol* 1997, 11, 573.
- Pizzi, A. *J Appl Polym Sci* 1997, 63, 603.
- Pizzi, A. *J Appl Polym Sci* 1999, 71, 517.
- Pizzi, A. *J Appl Polym Sci* 1997, 65, 1843.
- Pizzi, A.; Garcia, R.; Deglise, X. *J Appl Polym Sci* 1998, 67, 1673.
- Pizzi, A.; Probst, F. *J Appl Polym Sci* 1998, 67, 1341.
- Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1994.