

# Characterization of Crosslinking of Random Polymer Network by Rheological and Equilibrium Swelling Data

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## SYNOPSIS

The transesterification reaction in the molten state of ester groups of ethylene vinyl acetate (EVA) copolymers and ethylene acrylic ester (EMA) copolymers has been used to crosslink the chains of this polymeric system. The relative EVA copolymers (or EMA copolymers) concentration dependence of the network formation by co-crosslinking of EVA/EMA miscible blends has been assessed. EVA/EMA networks were characterized by swelling experiments, rheological measurements, and determination of the extent of the reaction through a chromatographic technique. All results can be compared in a master curve. The influence of the polydispersity and the microstructure of EVA and EMA samples was put in evidence. On the other hand, a scaling law ( $v_2 \sim M_c^{-3/5}$ ) was observed in agreement with predictions of the Flory-Rhener expression. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The phenomena of rubber elasticity have been under investigation for over a century. Thus, polymer systems can be converted to network structure by random crosslinking, which involves that network formation permanently renders some of the large-scale molecular arrangement of the uncrosslinked polymer. It is well known that the introduction of chemical crosslinks into a uncrosslinked polymer converts it from a viscoelastic liquid to a viscoelastic solid. For example, the transesterification reaction in the molten state of ester groups of ethylene vinyl acetate (EVA) copolymers and ethylene acrylic ester (EMA) copolymers leads to crosslink the copolymer chains.<sup>1</sup> In previous studies,<sup>1,2</sup> such a network constituting of 50% weight EVA and 50% weight EMA miscible copolymers was well characterized from chemical and rheological point of view.

This article is aimed in a first part to the characterization of crosslinking density by rheological data and by swelling degree at equilibrium for samples constituted by different weight concentration of EVA and EMA copolymers. Particular attention was paid to the contribution of the molecular weight

of uncrosslinked EVA/EMA polymer to the network structure. Moreover, several molecular models have been developed that predict the elastic and swelling behavior of the polymer network. Determination of crosslinking density of the polymer network by mechanical data in simple extension and by swelling degree at equilibrium was made.<sup>3</sup> Lastely, Patel et al.<sup>4</sup> and Malone et al.<sup>5</sup> showed that the Flory-Rhener<sup>6,7</sup> model, coupled with the phantom network model,<sup>8</sup> is in good agreement with swelling results when the experimentally measured elastic modulus is used in the analysis. Then, swelling and rheological results of EVA/EMA network were discussed and such results were used to calculate the polymer solvent interaction parameter  $\chi$  for EVA/EMA-tetrahydrofuran and EVA/EMA-toluene systems.

## EXPERIMENTAL SECTION

### Materials

EVA and EMA copolymers were kindly supplied by Atochem. The respective amount of acetate and acrylate groups contained in these copolymers is about 28 wt %, and the respective molecular weights for the EVA and EMA copolymers are as follows:  $M_w$  1 = 53.5 kg · mol<sup>-1</sup>,  $M_n$  1 = 19 kg · mol<sup>-1</sup>, and  $M_w$  2 = 94.3 kg · mol<sup>-1</sup>,  $M_n$  2 = 22 kg · mol<sup>-1</sup>.

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The microstructure of these copolymers was determined by  $^{13}\text{C}$  NMR spectroscopy. The quantitative distribution of the ester centered triads for the ethylene vinyl acetate copolymer is obtained from methyne carbons at  $\delta = 74$  (EVE—E: ethylene, V: vinyl acetate) and at  $\delta = 71.24$  and  $70.25$  (EVV); no VVV resonances expected at about  $\delta = 68$  ppm were observed. The detailed procedure is given in ref. 9, with the same solvent. Complete assignments have been previously done by Randall.<sup>10</sup>

The quantitative distribution of acrylate units A in ethylene methylacrylate copolymers has not yet been published. We first notice that the carbonyl resonances cannot be used for this purpose: in the range A = 9–35% weight, nearly the same pattern is observed, whereas an increase of EAA/EAE ratio is expected from 9 to 35% weight. Therefore, the splittings observed (175.40, 175.25, and 175.15) cannot be assigned to compositional EAA and EAE triads and remain unexplained. Then, we used the methyne carbon resonances previously assigned by Bruch.<sup>11</sup>

The results are the following: (1) ethylene vinyl acetate copolymers; sequences EVE, EVV, VVV, respectively, in % 95, 5, and 0; (2) ethylene methylacrylate copolymers; sequences EAE, EAA, AAA, respectively, in % 90.75, 7.95, and 1.30.

We can conclude that ethylene methylacrylate copolymer is more blocky than the ethylene vinyl acetate copolymer. The ethylene methylacrylate copolymers show a lower ratio of isolated ester unit and higher ratios of EAA and AAA triads.

### Network Preparation

The blend EVA/EMA/Catalyst was mixed in a twin screw extruder (Leistritz LSM30–34). The temperatures were regulated from  $130^\circ\text{C}$  at the feed zone to  $165^\circ\text{C}$  at the die. As described in a previous study,<sup>1</sup> at these temperatures and for the residence times inside the extruder ( $t \sim 200$  s), no crosslinking occurs.

The networks were formed in a molten state by curing between heating parallel plates: the chemical reaction of transesterification in the presence of dibutyltin oxide ( $\text{Bu}_2\text{SnO}$ ) was used to crosslink samples that were preliminary mixed in the extruder. This reaction has been well characterized in previous studies.<sup>1,12</sup> This exchange reaction of ester groups creates a covalent chemical link through an ester bridge between the chains of the two copolymers. Thus, such network contains tetrafunctional links only. A gas chromatography can be used to quantify the EVA/EMA network formation by titration of

methyl acetate, which is a volatile tracer of the reaction.

Swelling experiments of EVA/EMA networks were performed in toluene and tetrahydrofuran solvents: approximately 0.5 g of each sample was placed in 250 mL of solvent at the temperature of  $50^\circ\text{C}$ . After being sure that the swelling equilibrium had been reached (after 2 days in the solvent), the swollen network was weighed and dried under vacuum.

The changes in dynamic storage  $G'$  and loss  $G''$  moduli of EVA/EMA network during isothermal cure were followed in oscillatory shear mode using a rheometer mechanical spectrometer (RMS800) with the parallel plate geometry. The plates were 9 mm in diameter and the gap between the plates ranged from approximately 1 to 1.2 mm. Isothermal curing was performed at the frequency of 0.3 rad/s. In all cases, sample linearity response with respect to strain amplitude was verified. Strain amplitude was chosen in the range 50–1% on function of changes in dynamic modulus  $G^*$  with the network formation. Moreover, nitrogen gas was used to prevent thermal oxidation.

## RESULTS AND DISCUSSION

### EVA/EMA Network

#### *Rheological Characterization*

When the reaction of crosslinking occurs, the storage and loss moduli increase with time as the network results. At a particular point the storage and loss moduli cross. The crossover between  $G'(t)T_{\omega}$  and  $G''(t)T_{\omega}$  takes place at the same critical reaction time, within experimental error, independently of the frequencies applied. This critical point defined the gel point.<sup>13–16</sup> In addition to that, it was observed, as shown by frequency sweep curves of Figure 1, that a such network at gel point exhibits congruent moduli varying with frequency according to a power law,

$$G'(\omega) = G''(\omega) \sim \omega^{1/2} \quad (1)$$

in agreement with previous works of the literature on model networks.<sup>13–16</sup> The curves of the Figure 1 have been shifted horizontally by a factor  $A$  for easier comparison. Before tgel, the melt polymer is still in a liquid state and both moduli decrease to zero at low frequencies ( $G' \rightarrow \omega^2$  and  $G'' \rightarrow \omega$ ). Beyond the gel point, the shape of  $G'(\omega)$  and  $G''(\omega)$  change drastically as the reaction proceeds;  $G'$  and  $G''$  curves

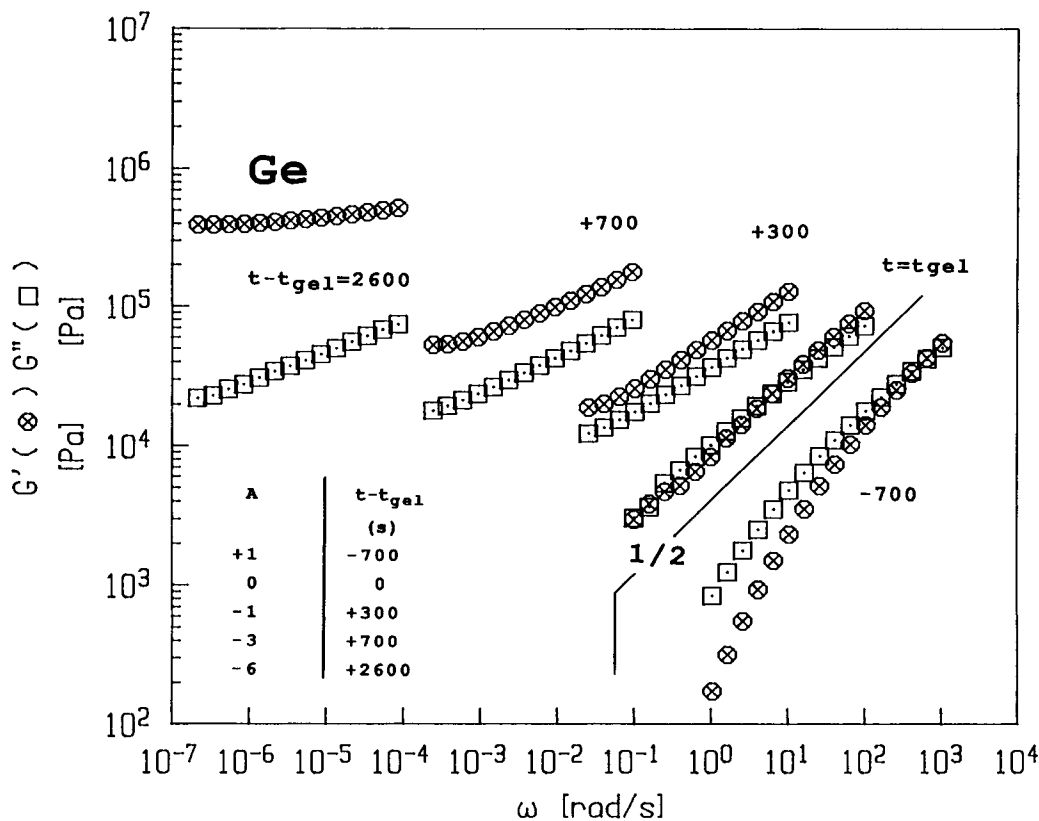


Figure 1 Variation of the storage and loss moduli at intermediate state of conversion, T = 170°C.

pass each other. Then at long curing time, the storage modulus  $G'$  tends towards a plateau at low frequency.

This plateau demonstrates the existence of permanent elasticity characteristics of a solid material and defined the equilibrium modulus  $G_e$  from rubber elasticity theories. Therefore, the value of this plateau also defined the crosslinking density of the network.

**Influence of EVA Concentration**

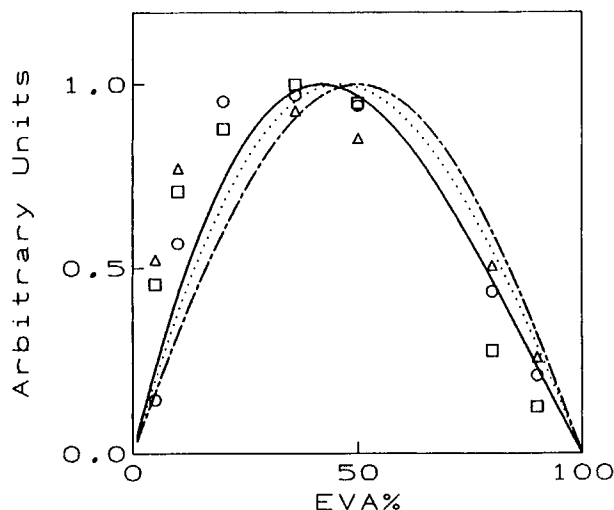
In previous works<sup>1,2</sup> only samples constituted by 50/50 by weight of EVA and EMA copolymers were studied. In order to establish if the EVA and EMA copolymers have a identical behavior in the EVA/EMA network formation, different concentrations of EVA in EVA/EMA samples were considered: 5/95; 10/90; 20/80; 36/64; 50/50; 80/20 and 90/10 At different times of the development of the crosslinking reaction, three techniques were used to quantify the EVA/EMA network: titration of methyl acetate, which allows access to the extent of the reaction, measurement of the equilibrium elastic modulus, and determination of the swelling degree

in tetrahydrofuran. The different results obtained from these three techniques can be compared on the same figure if the values obtained by each method are divided by the highest value. Consequently, variation of extent of the reaction  $p$ , equilibrium elastic modulus  $G_e$ , and network volume fraction at equilibrium swelling  $\nu_2$  change in the domain of arbitrary units in the range from zero to one. Experiments were carried out on networks that underwent curing time of 60 min at a temperature of 200°C.

As shown in Figure 2, an identical trend was observed in the variations of these different parameters vs. EVA concentration. Indeed, such behavior was expected in a first approximation: the equilibrium modulus can be assumed to be proportional to the extent  $p$  of the reaction from the theory of rubber elasticity<sup>5</sup> if one assumes that only the network strands give rise to the rubber elasticity force (affine model)

$$G_e = \nu RT \text{ with } \nu \sim p \tag{2}$$

Where  $\nu$  is the concentration of elastically active strands,  $R$  the gas constant, and  $T$  the absolute temperature.



**Figure 2** Variations of characteristic parameters of the network vs. EVA concentration: ( $\square$ ) methyl acetate titration, ( $\blacktriangle$ ) equilibrium modulus, and ( $\circ$ ) equilibrium swollen.

Modelization: (—) Kinetic law of 2nd order (relation 6); (·····) previous modelization with effect of EMA microstructure; (---) previous modelization with effect of molecular weight distribution of EVA/EMA uncrosslinked sample.

From this last equation, the average molecular weight  $M_c$  between two chemical crosslinks can be estimated from value of the plateau modulus:

$$M_c = \rho \frac{RT}{G_e} \quad (3)$$

where  $\rho$  is the polymer density.

On the other hand, molecular weight between crosslinks can be related to swelling degree at equilibrium from a scaling law proposed by de Gennes on the  $c^*$  theorem.<sup>17</sup> The  $c^*$  theorem predicts in semidilute polymer solution:

$$c^* \sim M^{-4/5} \quad (4)$$

where  $M$  is the molecular weight of the polymer chains.

Then, this theorem is based on an analogy between semidilute polymer solutions and equilibrium swollen polymer network:

$$\rho v_2 \sim c^* \quad (5)$$

Assuming in a network that  $M = M_c$ , the  $c^*$  theorem will write finally:

$$\rho v_2 \sim M_c^{-4/5} \quad (6)$$

However, there are still ongoing studies about the applicability and the validity of the  $c^*$  theorem. Patel et al.<sup>4</sup> observed experimentally a power law  $v_2 \sim M_c^{-0.4}$  in the case of model and imperfect networks, whereas Oikawa et al.<sup>18,19</sup> reported good agreement with the theorem. They observed an exponent of  $-0.71$ , which is close to the theorem predictions of  $-4/5$ . However, this last result seems to be experimentally fortuitous.

On the other hand, Figure 2 put in evidence that EVA and EMA copolymers have not a symmetric behavior in the formation of the EVA/EMA network. This phenomenon may be due to the different microstructure of the EVA and EMA samples that induce the formation of the EVA/EMA networks having different structures. For the concentrations of EVA lower than 50% (EMA > 50%), EVA chains act in the system as crosslinking agents of EMA chains, and vice versa, for the concentration of EVA higher than 50%, EMA chains act in the network as crosslinking agents. On the other hand, NMR experiments indicate that EVA copolymers obey a isolated repartition of vinyl acetate reactive sites, whereas EMA copolymers obey rather a block repartition of methyl acrylate copolymers. From this point of view, a dissymmetric behavior of EVA and EMA copolymers on the formation of the EVA/EMA network may be admitted.

### Modelization

As generally assumed, the reactions of transesterification are second order. Then, in a previous study<sup>1</sup> we showed that the kinetic law can be expressed as:

$$p = x/a = \frac{1 - \exp((a-b)k_1t)}{1 - \frac{a}{b} \exp((a-b)k_1t)} \quad (7)$$

where  $a$  and  $b$  ( $a \neq b$ ) were the respective initial concentrations of acetate and acrylate groups in the molten state.  $M(t)$  was defined as a damping function that takes into account the mobility of the polymer chains as a network results and was expressed as:

$$M(t) = P_\infty (1 - \exp(-t/\tau)) \quad (8)$$

Values of  $k_1$ ,  $\tau$ , and  $p_\infty$  were calculated in a particular case where  $a = b$ .<sup>1</sup> It was shown that  $\tau$  may be correlated to gel time and  $p_\infty$  is a characteristic parameter of the network. It defined the maximum of crosslinking density that the network can reach at long times. It was found to be independant of the

temperature. Figure 2 reports the variations of this kinetic law. Obviously, such a kinetic law predicts a symmetric behavior of the EVA and EMA copolymers in the EVA/EMA network. Nevertheless, as pointed out previously, EMA copolymers are more blocky than EVA copolymers. Then, the effective concentration of the active reactive sites of acrylic ester groups may be assumed smaller than the concentration of effective sites of acetate ester groups. For example, Figure 2 plots the prediction of the kinetic law, assuming that only 90% of acrylic ester groups are effectively reactive in the reaction of crosslinking. As expected, a dissymmetric behavior of EVA and EMA copolymers was obtained. However, Figure 2 shows that this assumption is not sufficient.

Actually, EMA copolymers present a broader molecular weight distribution than EVA copolymers do as underlined in the material part. As EVA and EMA copolymers are compatible, the molecular weight distribution of the EVA/EMA sample can be written as:

$$M_w = \phi M_{w1} + (1 - \phi) M_{w2}$$

$$\frac{1}{M_n} = \frac{\phi}{M_{n1}} + \frac{1 - \phi}{M_{n2}} \quad (9)$$

where  $\phi$  is the weight concentration of EVA copolymer in the network. Then, the molecular weight distribution of the uncrosslinked EVA/EMA sample depends on the EVA concentration. On the other hand, the theory of rubber elasticity predicts that the extent of the reaction at gel time is dependent of the average molecular weight of the polymer chains:

$$p_{gel} = \frac{1}{X_w} \quad \text{with} \quad X_w \sim M_w \quad (10)$$

Where  $X_w$  is the weight average of crosslinkable sites.

Then, from this point of view, the crosslinking network formation depends in part on the molecular weight distribution, and one can assume that the parameter  $p_{\infty}$ , which is a characteristic parameter of the network, obeys the following relation of proportionality:

$$p_{\infty} \sim M_w \quad (11)$$

Figure 2 shows the predictions of the kinetic law that takes into account the correction of the effective reactive sites (dotted line) coupled with the correction of the polydispersity effect on the EVA/EMA

network formation (solid line). Although a slight difference remains for the lower concentration of EVA, a good agreement was observed as a whole.

Then, the predictions of the kinetic law prove that the formation of a polymer network is largely sensitive to the repartition of the effective reactive sites along the polymer chains and to the molecular weight distribution of the uncrosslinked polymer chains.

## EQUILIBRIUM SWELLING BEHAVIOR

As previously reported, the principal result of the rubber elasticity<sup>5</sup> approach was the prediction of the shear modulus is approximately proportional to the number  $\nu$  of mol of elastic strands per unit volume of the network. Then, the affine network model results in Eq. (2) ( $Ge = \nu RT$ ).

For the phantom network,<sup>7</sup> the junctions (chemical crosslinks) are free to fluctuate and the shear modulus is lower than that of an affine network:

$$Ge = (\nu - \mu)RT \quad (12)$$

where  $\mu$  is the number of mol of junctions per unit volume of the network.

In order to take into account the contribution to the modulus from polymer chain entanglements, a phenomenological model was developed by Langley<sup>20</sup> and Dossin and Graessley.<sup>21</sup> The model can be expressed as:

$$Ge = (\nu - \mu h)RT + G_N^0 Te \quad (13)$$

where  $G_N^0$  is the plateau modulus of the uncrosslinked polymer melt.  $Te$  is a trapping factor,  $h$  is an empirical parameter between zero and one. In a previous study, we have shown<sup>1</sup> in the case of EVA/EMA network that  $h = 0$  and  $G_N^0 = 6 \times 10^5$  Pa. On the other hand, values of  $Te$  were calculated using relations derived by Pearson and Graessley.<sup>22</sup> Table I indicates that trapping entanglements is significant and must be taken into account in the development of swelling behavior of polymer networks.

Several molecular models have been developed that predict the elastic and swelling behavior of polymer networks. A review of various models that predict the extent of swelling that the network undergo when placed in good solvent was made by S. K. Patel et al.<sup>4</sup> In particular, they found that Flory-Rhener<sup>7</sup> model coupled with the phantom network (relation 12) predicts the experimental

**Table I** EVA/EMA Network Parameters: Extent of the Crosslinking Reaction  $p$ 

$p \times 10^{+2}$	$\nu_2\text{THF} \times 10^{+1}$	$\nu_2\text{tol} \times 10^{+1}$	$Ge(\text{Pa}) \times 10^{-5}$	$Te \times 10^{+1}$	$\chi\text{THF} \times 10^{+1}$	$\chi\text{tol} \times 10^{+1}$
0.1	0.8	—	2.3	2.7	2.07	—
2.9	1.12	1.00	3.6	3.0	2.48	0.98
4.5	1.41	1.17	4.4	4.5	3.15	0.90
6.0	1.60	1.35	5.75	5.0	3.09	1.10
7.4	1.89	1.54	7.2	5.2	3.33	1.20
8.1	1.92	1.75	8.97	5.4	2.86	1.25
8.7	2.17	1.82	10.3	6.0	3.16	0.95
9.7	2.27	2.00	11.0	6.5	3.23	1.44
12	2.38	2.08	12.0	7.0	3.26	1.39
14	2.50	2.13	13.0	7.3	3.32	1.23

Polymer volume fraction at equilibrium swelling in tetrahydrofuran  $\nu_2\text{THF}$  and toluene  $\nu_2\text{tol}$  solvent. Equilibrium shear modulus  $Ge$ ; trapping entanglement factor  $Te$  and the polymer interaction parameters  $\chi\text{THF}$ ,  $\chi\text{tol}$ .

swelling results of imperfect network when the experimental value of the equilibrium elastic modulus is used. They obtained:

$$-\left[\frac{\ln(1-\nu_2) + \nu_2 + \chi\nu_2^2}{V\nu_2^{1/3}}\right] = \frac{Ge}{RT} \quad (14)$$

This equation is a direct prediction of the original postulate of Flory and Rehner that swelling is determined by a balance between osmotic and elastic force. On the other hand, effects of trapped entanglements on swelling are include by this equation.

Then, this expression can be solved for  $\chi$  and thereby to calculate values of  $\chi$  as a function of  $\nu_2$

in the case of networks constituted by weight of 50% of EVA and 50% of EMA. The resulting values of  $\chi$  are reported in Figure 3 for toluene and tetrahydrofuran solvents.

Linear regression to the data of this figure for tetrahydrofuran yields:

$$\chi = 0.19 + 0.62\nu_2 \quad (15)$$

In the case of toluene the best fit line gives:

$$\chi = 0.059 + 0.345\nu_2 \quad (16)$$

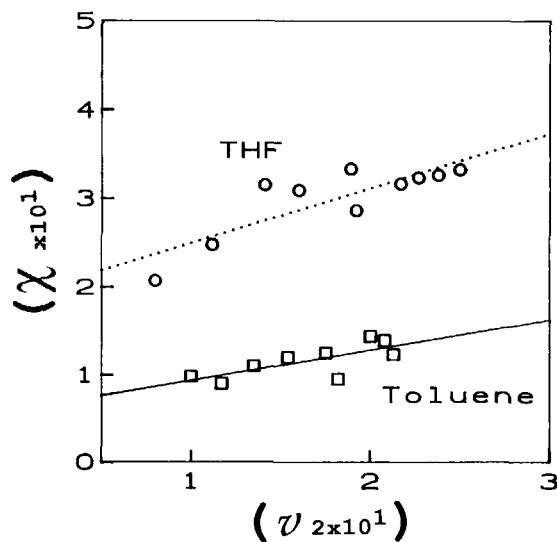
These results mean that toluene is a better solvent of the EVA/EMA polymers than tetrahydrofuran.

The average molecular weight  $M_c$  between two effective crosslinks (chemical crosslinks plus topological trapped entanglements) can be calculated according to the affine model from the experimental value of the equilibrium modulus according to Eq. (3).

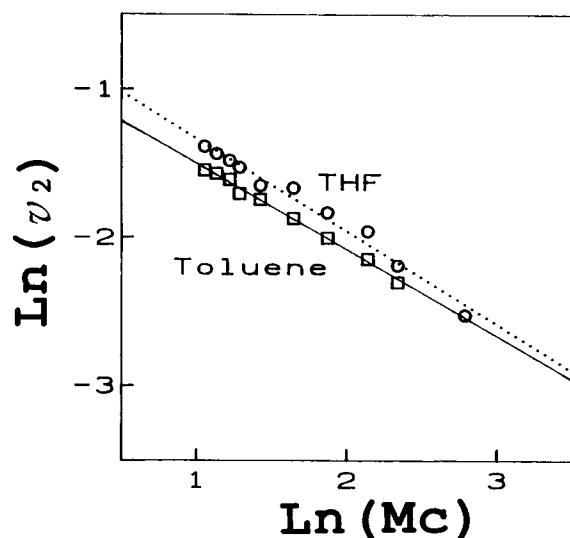
In Figure 4 are plotted  $\log(\nu_2)$  vs.  $\log(M_c)$  for the networks that were swollen in THF and toluene. The data can be fitted quite well with a straight line of 0.63 and 0.58, respectively. As already observed in the literature<sup>4</sup> on model and imperfect network, the exponent of the power law is very different from the scaling law prediction based on  $c^*$  theorem. However, these results are reasonably close to results of Flory-Rhener in the limit of  $\nu_2 \ll 1$ .

$$\nu_2 \sim M_c^{-3/5} \quad (17)$$

Then, these results show that the Flory-Rehner expression gives a good prediction of scaling law on network formed from random crosslinking of polymer chains of high molecular weight.



**Figure 3** Determination of the polymer solvent interaction parameter from relation 14. (○) Tetrahydrofuran solvent and (□) toluene solvent.



**Figure 4** Variation of equilibrium swollen network vs. average molecular weight between two crosslinks. The symbols are the same as in the Figure 3.

## CONCLUSIONS

The relative EVA copolymers (or EMA copolymers) concentration dependence of the network formation by co-crosslinking of EVA/EMA miscible blends has been assessed. Such a network, which forms through an exchange reaction of ester groups of the two copolymers, contains tetrafunctional links only. EVA/EMA networks were characterized by swelling experiments, rheological measurements, and determination of the extent of the reaction through chromatographic technique. In a first approximation, all results can be compared in a master curve. On the other hand, prediction of these results through a kinetic law of second order of the crosslinking reaction was attempted. A good prediction was obtained taking into account, in one hand, that the EMA copolymer was less statistic than EVA copolymer from repartition of reactive sites point of view, and the other hand, that EMA copolymers presents a broader molecular weight distribution than EVA copolymers.

In a second part, the elastic behavior and equilibrium swelling of networks constituted of 50% EVA and 50% EMA were studied. Average network parameters were calculated from expression derived by Pearson and Graessley.<sup>22</sup> These results show that topological entangling interactions can strongly influence the equilibrium elastic modulus through the network parameter  $Te$ . According to the Flory-Rhener model, coupled with the phantom network assumption, the interaction parameter  $\chi$  was calculated in tetrahydrofuran and toluene solvents. On the

other hand, a scaling law ( $v_2 \sim M_c^{-3/5}$ ) was observed in agreement with predictions of the Flory-Rhener expression.

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