

Mechanical and Gas Transport Properties of Poly- ϵ -caprolactone Model Networks

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Synopsis

The glass transition temperature increases with increasing crosslink densities in model networks formed by endlinking poly- ϵ -caprolactone with a triisocyanate crosslinking agent. In the noncrystalline networks, the gas permeability decreases with increasing crosslink density. These results are consistent with an interpretation that the crosslinks reduce the main-chain molecular motions which are important to these processes. At the lowest crosslink density, where poly- ϵ -caprolactone networks are crystalline, the gas permeability is lower than would be expected based on the volume fraction of amorphous polymer. The excess reduction in permeability is attributed to crystallization-induced enrichment of crosslink junction points in the amorphous fraction of the network. This reduces the permeability by creating an artificially high crosslink density in those regions of the network responsible for gas transport. Since crosslinking increases the stiffness and reduces the flexibility of the network polymer chains, it affects large penetrants more strongly than small ones. Therefore, increasing the crosslink density proves to be a useful method for increasing gas separation factors.

INTRODUCTION

Main-chain flexibility and segmental mobility of polymer chains help determine the permeability of gases in glassy polymers.¹ It is not surprising, therefore, that modifications of polymers which alter main-chain molecular motions (such as crystallization, orientation, plasticization, and crosslinking) also cause changes in the gas transport characteristics of the polymer.^{2,3} Modification of polymers by crosslinking is of particular interest because it imparts high physical strength, dimensional stability, and solvent resistance to the polymers. All of these properties are required of polymers used in practical gas separation systems. Unfortunately, the decrease in permeability which usually accompanies crosslinking can sometimes limit the use of crosslinked polymer in applications requiring specified permeability characteristics (e.g. gas separations,⁴⁻⁶ packaging,⁷ and biomedical applications⁸).

Several previous studies on randomly crosslinked polymers showed a general decrease in the permeability P with increasing crosslink density.⁹⁻¹¹ In a recent paper on model networks of poly(propylene glycol) we established that the logarithm of P decreased linearly with \overline{M}_c^{-1} , where \overline{M}_c is the number-average molecular weight between crosslinks.¹² In that study, the use of a noncrystalline polyether avoided any complications in interpretation of gas transport data which might have arisen due to the presence

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of crystallinity in the networks. Many polymers, however, do crystallize. For this reason we have examined the dynamic mechanical and gas transport properties of the model networks of the crystallizable polymer, poly- ϵ -caprolactone.

EXPERIMENTS

The NIAX Polyol PCP series of poly- ϵ -caprolactone polyols were obtained from Union Carbide Corp. The crosslinking agent, a tris(*p*-isocyanatophenyl thiophosphate), Desmodur RF, was obtained from Mobay Chemical Corp. The polyols were dried *in vacuo* overnight and mixed with stoichiometric quantities of the crosslinking agent (dissolved in methylene chloride). The mixtures were warmed to $\sim 50^\circ\text{C}$ for a few minutes and poured into Teflon-lined molds. The molded films were compressed at ~ 300 psi at room temperature and allowed to cure for 24 h. To ensure complete crosslinking, the sheets were removed from the mold and heated at 50°C under a dry N_2 purge for an additional 3–4 h.

The dynamic mechanical measurements were made in an automated Rheovibron DDV II. All measurements were made in N_2 , at 11 Hz, over a temperature range of -160°C to 240°C , and at a heating rate of $\sim 1^\circ\text{C}/\text{min}$. Premeabilities were determined for the individual components of two binary gas mixtures; H_2/CO (25.1% H_2) and H_2/CH_4 (25.5% H_2). The total gas permeability at 22°C was determined for each gas mixture, and then the permeate was analyzed by GLPC to determine its composition. Details of the apparatus and the procedure for determining the permeability of components of binary gas mixtures have been described previously.¹²

RESULTS AND DISCUSSION

Dynamic Mechanical Properties

The dynamic mechanical loss curves for the networks of poly- ϵ -caprolactone are shown in Figure 1. The T_g and $\tan \delta_{\text{max}}$ data are given in Table I. The data show three general trends: (i) $\tan \delta$ curves are broad at low crosslink densities and become sharper as the crosslink density increases; (ii) $\tan \delta_{\text{max}}$ increases with increasing crosslink density; and (iii) the T_g increases with increasing crosslink density.

Poly- ϵ -caprolactone is a crystalline polymer,¹³ and at low crosslink densities, the X-ray diffraction spectra show the presence of crystallinity in the poly- ϵ -caprolactone networks as well. Networks (1) and (2) have crystallinities of 30% and 4%, respectively. The $\tan \delta$ loss curves for the crystalline samples are weak and quite broad, analogous to those for crystalline poly- ϵ -caprolactone¹³ and for poly(ethylene terephthalate) (PET).¹⁴ In unoriented PET, $\tan \delta_{\text{max}}$ decreases if the sample is annealed prior to measurement; the decrease being greatest at the highest annealing temperatures. The latter result has been attributed to the increased crystallinity which accompanies thermal treatment of PET.¹⁴ In fact, an empirical relationship has been proposed for determining the degree of crystallinity of PET based on the decrease in $\tan \delta_{\text{max}}$ values.¹⁵ The reduction in the intensity of the mechanical loss in polymers with partial crystallinity reflects the restraints

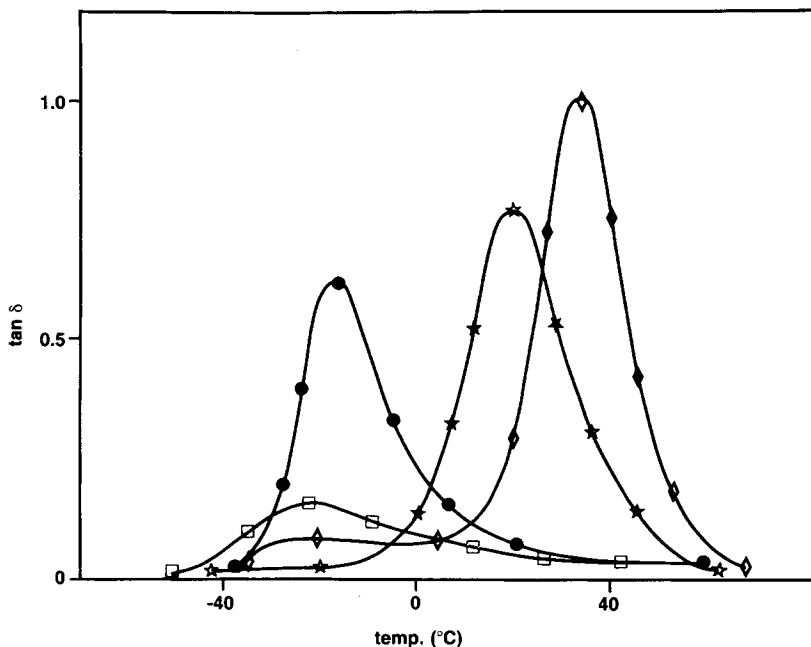


Fig. 1. Dynamic mechanical loss curves for networks of poly- ϵ -caprolactone. The network parameters are given in Table I. (Some of the data points are not shown in order to improve clarity.) Network: (\square) 1; (\bullet) 2; (\star) 3; (\blacklozenge) 4.

imposed on the segmental mobility of the amorphous polymer chains by the crystallites. The degree of restraint depends on the crystallinity index and the size and distribution of the crystallites.¹⁴ Below we give evidence to suggest that the crosslink junction points are concentrated into the amorphous regions of the crystalline networks. This would tend to reduce further the average segmental mobility of the polymer chains in the amorphous regions.

X-ray diffraction spectra of networks (3) and (4) show no crystalline reflections, suggesting that high crosslink densities in poly- ϵ -caprolactone networks disrupt the molecular packing and hinders the formation of crystallites. $\tan \delta_{\max}$ continues to increase as the crosslink density increases.

Figure 2 shows the T_g vs. \bar{M}_c^{-1} for the poly- ϵ -caprolactone networks and the general trend of T_g increasing with increasing crosslink density. Also shown in the figure is a line representing the T_g data for poly(propylene

TABLE I
Properties of the Poly- ϵ -caprolactone Model Networks

Network	\bar{M}_c^a	T_g^b (°C)	$\tan \delta_{\max}$	Crystallinity ^c index
1	2000	-19.1	0.15	0.30
2	1250	-17.7	0.63	0.04
3	875	19.7	0.77	0.00
4	530	34.4	1.00	0.00

^a Assumed to be the \bar{M}_n of the uncrosslinked polymer.

^b Dynamic mechanical measurement at 11 Hz.

^c Obtained by XRD method using sheets of network.

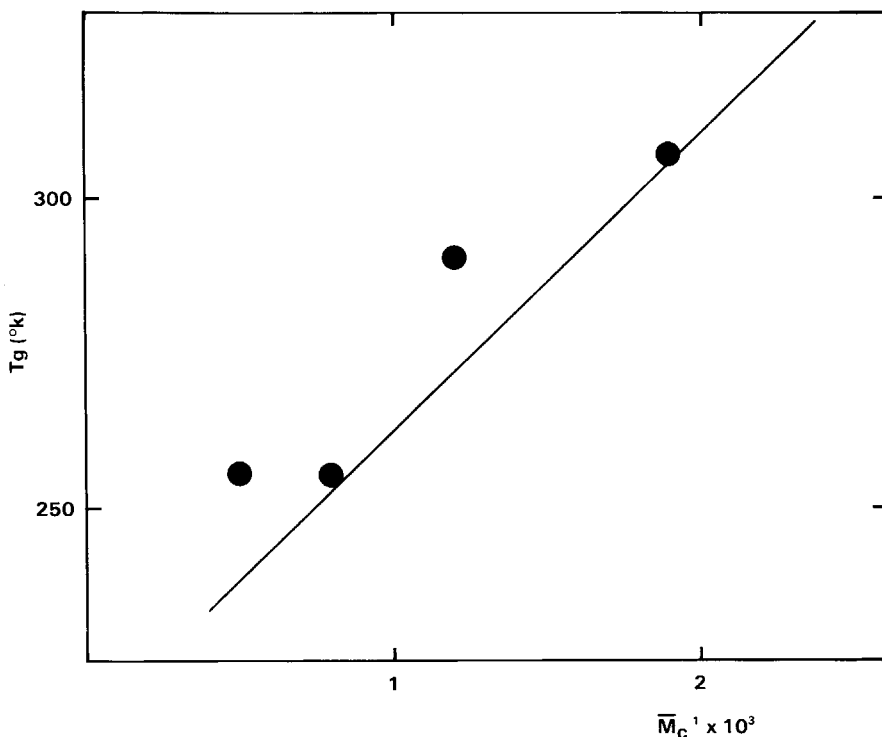


Fig. 2. Dependence of the glass transition on \bar{M}_c^{-1} for poly- ϵ -caprolactone networks. The solid line represents the T_g of poly(propylene glycol) networks from Ref. 16.

glycol) networks used in an earlier study.¹⁶ For the poly(propylene glycol) networks, part of the increase in T_g with crosslinking was attributed to the decreased mobility of the network chain segments between crosslinks, and part was attributed to the incorporation of the crosslinking agent. The presence of crystallinity causes slight to moderate increases in the T_g for many polymers,¹⁷ and should do so for networks as well. The T_g of the crystalline form of poly- ϵ -caprolactone is reported to be 11–16°C greater than the amorphous form.¹³

Gas Transport Properties

Mechanical loss and gas transport phenomena in polymers both depend upon polymer segmental mobility, so changes in the dynamic mechanical properties with crosslinking should augur changes in gas transport properties as well. A correlation has already been observed between segmental mobility and gas transport in amorphous poly(propylene glycol) networks,¹² polyesters and copolyesters,¹⁸ substituted polystyrenes,¹⁹ and plasticized poly(vinyl chloride).²⁰

Crosslinking a crystallizable polymer may change its gas permeability for three reasons: (i) due to restrictions of chain mobility brought about by physical crosslinking process; (ii) due to a "copolymer effect"¹⁶ from incorporating a crosslinking agent into system; and (iii) due to changes in crystallinity which may be influenced by the crosslinking density. We have

shown that the first two effects cause the permeability of poly(propylene glycol) networks to decrease with increasing crosslink density.¹² As for the third effect, we expect an increase in crystallinity to decrease permeability, since gas permeation is eliminated in the crystalline regions and reduced in the adjoining amorphous regions due to the restricted mobility of the polymer chains.

Figure 3 shows plots of the permeability of poly- ϵ -caprolactone networks to several gases as a function of crosslink density. The permeabilities were determined from binary gas mixtures of H₂/CO and H₂/CH₄ at 22°C and are given in Table II. The permeability of H₂ in the presence of CO is slightly greater than in the presence of CH₄. In both cases, P_{H_2} shows a similar dependence on the crosslink density.

Ignoring for now the results from the highly crystalline network (1), the decrease in permeability with increasing crosslink density in the poly- ϵ -caprolactone networks is similar to the trend observed in poly(propylene glycol) networks.¹² The permeabilities for the various gases depend on their gas solubility and diffusion coefficients. In this series of networks, which are chemical similar, we expect the gas solubility to be roughly constant across the series.¹¹ A decrease in permeability must therefore principally result from a decrease in the diffusion coefficient as the crosslinks reduce the frequency and/or amplitude of the cooperative molecular motions in the amorphous polymer.

Separation factors determined from binary gas mixtures are given in Table II. Since the diffusion coefficient depends on the activation energy for separation of adjacent polymer chains over a distance equal to the penetrant diameter,²¹ reducing chain flexibility by crosslinking has the greatest effect on large diameter penetrants. Separation of small molecules from large ones will be enhanced with increasing crosslink density. High values for separation factors for H₂/CO and H₂/CH₄ at the highest crosslink densities are consistent with the discussion above. This appears to be a general phenomenon. Separation of H₂ from CO is also greatest at the highest crosslink densities in poly(propylene glycol) networks.¹² Modifications of polymers by addition of low-molecular-weight additives²⁰ or by exposure to gamma radiation²² show greater effect on large penetrants than on small ones.

Turning now to the results for the crystalline network (1), Michaels and co-workers^{23,24} have shown that the reduction in solubility and diffusion coefficients in crystalline polyethylene is dependent on factors such as volume fraction of amorphous polymer, the shape and size of crystallites, and the diameter of the penetrant. In the simplest approximation, both the solubility and the diffusion coefficients are reduced by the volume fraction of the crystals. Thus, an estimate for the reduced permeability \bar{P} in a semi-crystalline polymer is given by^{25,26}

$$\bar{P} = P_a \times V_a^2 \quad (1)$$

where P_a is the permeability and V_a is the volume fraction of amorphous polymer. Equation (1) predicts a reduction of about 50% in the gas permeability for network (1) due to crystallinity. The actual permeabilities for

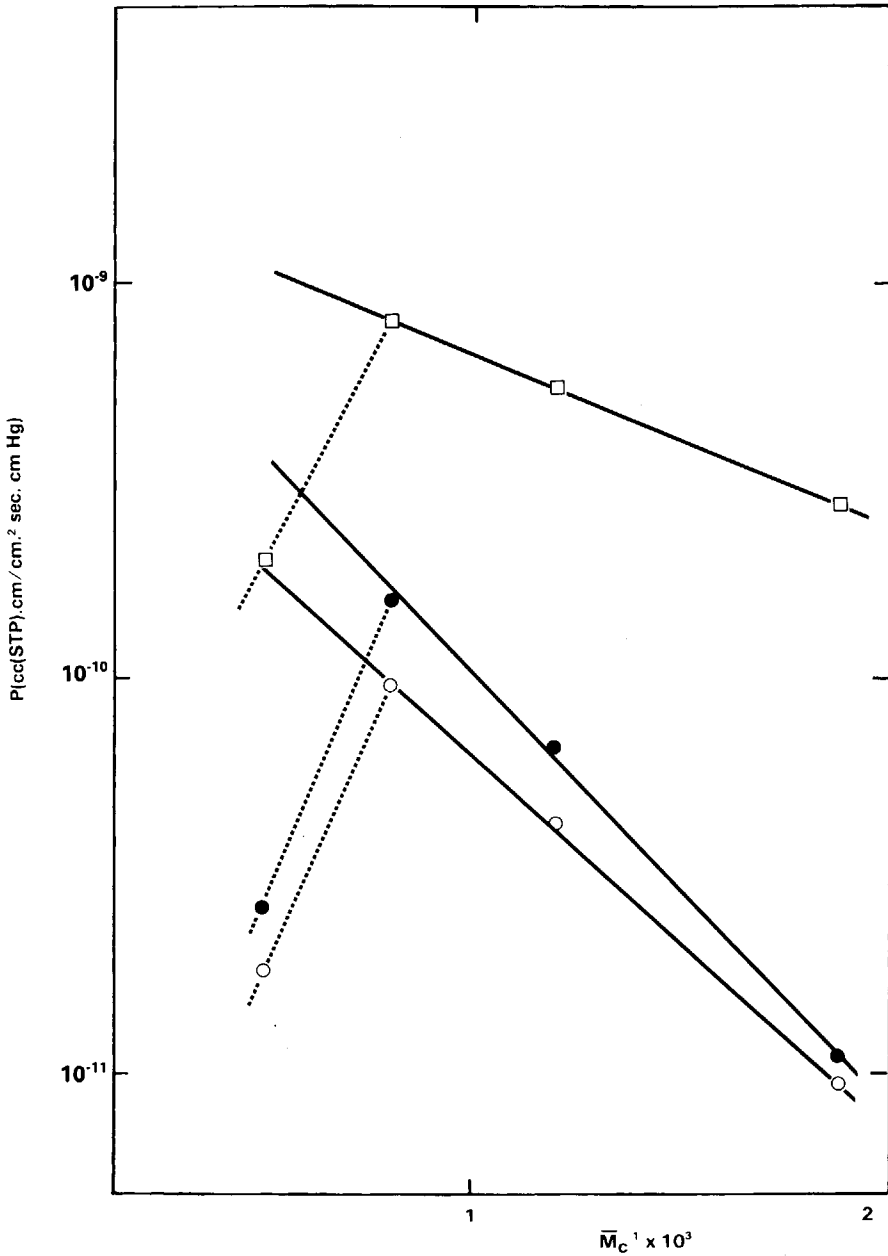


Fig. 3. Dependence of gas permeabilities on \bar{M}_c^{-1} for poly- ϵ -caprolactone networks at 22°C. The data for H₂ (□) and CO (○) are from a H₂/CO gas mixture; the data for CH₄ (●) are from a H₂/CH₄ mixture.

TABLE II
 Gas Permeability of the Poly- ϵ -caprolactone Model Networks

Network	Mixture H ₂ -CO ^a			Mixture H ₂ -CH ₄ ^b		
	Permeability ^c		Separation factor, H ₂ /CO	Permeability ^c		Separation factor, H ₂ /CH ₄
	H ₂	CO		H ₂	CH ₄	
1	1.94	0.191	10.18	1.68	0.230	7.32
2	8.10	0.970	8.35	6.73	1.33	5.07
3	5.26	0.432	12.2	5.29	0.642	15.4
4	2.86	0.095	30.1	2.55	0.100	25.5

^a Feed composition 25.1% H₂ in CO; feed pressure 350–375 cm Hg.

^b Feed composition 25.5% H₂ in CH₄; feed pressure 350–375 cm Hg.

^c Units = 10¹⁰ × cm³ (STP) cm/cm² · s cm Hg measured at 22°C.

H₂, CO, and CH₄ are reduced by 82%, 90%, and 92% of the values that would be expected for a noncrystalline network of the same crosslink density (see Fig. 3).

Like branched polymers¹⁷ and copolymers,²⁷ crystallinity in networks develops along sequential crystallizable repeat units; the longer the sequence is, the more stable the crystal. Branch points, comonomers, and crosslink points are all thermodynamically excluded from crystals.²⁷ Because crosslink points are excluded from the crystals, this effectively increases the crosslink density in the amorphous regions where gas transport occurs. With the aid of eq. (1) and parameters for network (1), ($\bar{P}_{\text{H}_2} = 1.94 \times 10^{10}$ cm³ (STP) cm/cm²·s cm Hg and $V_a = 0.7$), the effective hydrogen permeability in the remaining amorphous region must be about 4×10^{10} cm³ (STP) cm/cm²·s cm Hg. Referring to Figure 3, this effective hydrogen permeability corresponding to an effective $\bar{M}_c = 660$. By the same method, the effective \bar{M}_c of network (1) for CO and CH₄ is about 800. At first glance, these seem to indicate rather high effective crosslink densities. Of course, 30% of the polymer repeat units in the network are excluded from the amorphous fraction as crystals. The difference between the expected \bar{M}_c of 1400 (30% of 2000) and the calculated effective \bar{M}_c of 660–800 must be a measure of the influence that the crystals have on diffusion through the remaining amorphous region. This is reasonable. Recall that the crystallites also act as anchors for the amorphous chain segments, so that every chain entry point has a similar effect on molecular dynamics as has a crosslink junction point. If one assumes that 30% of the repeat units in the *center* of every chain are incorporated into crystals, then the molecular weight between crosslinks and crystals would be 700. More likely, the chains are randomly incorporated into crystals. Nevertheless, the *average* effective molecular weight between "crosslinks" would be 700, in good agreement with the effective \bar{M}_c determined empirically.

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Received December 2, 1983

Accepted March 2, 1984