Isobaric and isochoric fragilities and the influence of volume on the temperature dependence of local segmental relaxation in polyvinylethylene networks

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The ratio of the isochoric and isobaric activation enthalpies at T_g is used to quantify the relative contributions of the specific volume and temperature to the local segmental dynamics of polyvinylethylene networks. The dynamics of the networks become more dominated by temperature with increasing cross-link density, consistent with an increasing isobaric fragility. We also find a correlation between the isochoric and isobaric fragilities for the polyvinylethylene networks, in accord with a previously reported relationship between these two quantities for polymers and molecular glass-forming liquids [R. Casalini and C. M. Roland, Phys. Rev. E **72**, 031503 (2005)]. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2135787]

INTRODUCTION

A common treatment of polymers is their cross-linking to form a network from the viscous melt. Especially for polymers having a glass transition temperature T_g below ambient, cross-linking is essential for shape retention and high elasticity without creep. The effect of network formation on properties has been investigated for a very long time, with a particular focus on the mechanical behavior. Starting from the original "ideal" rubber elasticity models,[1–3] the modern view has emerged of the mechanical properties of networks arising from the competing effects of chain configurational entropy and intermolecular constraints on the chains.[4,5] While rubber elasticity theories are well developed, they only address the mechanical equilibrium behavior, notwithstanding the connection between the equilibrium and relaxation properties. The same microscopic motions studied directly by relaxation spectroscopies underlie the elastic properties of the network. Some connections can be drawn between the analyses of network elasticity theories and models of the local segmental dynamics of polymers.[6,7] These can potentially yield more fundamental insights into structure-property relationships in cross-linked polymers.

The general effects of cross-linking on segmental relaxation are well known: an increased and broadened glass transition[8] and local segmental relaxation times τ_α that are more sensitive to temperature (more fragile).[9] It is not clear whether other characteristic properties, especially those observed at higher frequencies and involving short length scales, such as the dynamic crossover, would be significantly influenced by the network structure. Some effects of network formation on the Johari-Goldstein secondary process in epoxy resins have been described.[10] Herein we address one particular aspect of the glass transition—the degree to which the change of the local segmental relaxation times with temperature is governed by temperature changes *per se*, as opposed to the accompanying changes in volume. For molecular glass formers, volume (or density) effects are substantial; typically half the T dependence of τ_α is due to changes in volume. However, for polymers, volume effects are weaker. This is a consequence of the large degree of intramolecular bonding. Intramolecular bonds are insensitive to pressure or density (as seen, for example, in the weak pressure dependence of the dielectric strength of the normal mode in type-A polymers[11]), so that thermal contraction exerts only a weak effect on the local segmental dynamics.

These factors governing $\tau_\alpha(T)$ can be quantified from the ratio of the isochoric, $E_V(\equiv R(d\ln\tau/dT^{-1})|_V)$ and the isobaric, $E_P(\equiv R(d\ln\tau/dT^{-1})|_P)$, activation enthalpies.[12] For small molecules, the ratio ranges from 0.38 to 0.64 while for polymers the ratio goes as high as 0.81, with most values greater than 0.5.[13,14] The latter signifies equal contributions from volume and thermal energy to $\tau_\alpha(T)$.

The importance of these contributions is that they go to the heart of theories of the glass transition. Free volume models[15,16] posit empty space as the parameter controlling local motion, whereby $E_V/E_P \sim 0$. On the other hand, energy landscape approaches[17,18] focus on the effect of thermal energy in circumventing potential barriers and in the limit imply $E_V/E_P \sim 1$.[19] Obviously neither view is strictly correct. Entropy models of the glass transition[20,21] make no explicit prediction for E_V/E_P. Moreover, they suffer from the absence of values for the configurational entropy determined directly from experiment, without reliance on approximations.

In this work we analyze the segmental dynamics of polyvinylethylene (PVE) networks prepared using varying levels

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TABLE I. Polyvinylethylene networks.

Peroxide (%)	N	T_g (C)[a] PVT	T_g (C)[a] Dielectric[d]	α_P (C^{-1})[b]	B (GPa^{-1})[b]	G (MPa)[c]	E_V/E_P[b]
0	⋯	−10.8	−0.5	7.016×10^{-4}	0.43	940	0.78±0.01
0.056	150	−0.1	3.7	6.243×10^{-4}	0.48	840	0.81±0.01
0.222	28	13.5	9.6	4.143×10^{-4}	0.47	770	0.83±0.01
0.444	21	12.0	12.1	4.081×10^{-4}	0.46	670	0.85±0.01
0.666	(2)	14.7	14.6	3.627×10^{-4}	0.45	640	0.83±0.01

[a]At P=0.1 MPa.
[b]At T_g and P=0.1 MPa.
[c]At $T\sim T_g-15$ and P=0.1 MPa.
[d]Reference 9.

of dicumyl peroxide. Free radical cross-linking of this polymer is accompanied by chain reaction, yielding high-functionality cross-links; constraining effects of the network junctions are thereby amplified. Previously dielectric spectroscopy was used to measure τ_α as a function of temperature for PVE networks of varying cross-link density.[9] Herein we report pressure-volume-temperature (PVT) measurements on PVE samples which are equivalent to the prior materials. From the analysis, in combination with the earlier $\tau_\alpha(T)$ data, we determine the relative contribution of volume and temperature to the segmental dynamics and how this varies with the degree of cross-linking. We also use the data on the PVE networks to assess two recently reported linear correlations of the isobaric fragility with, respectively, the isochoric fragility[22] and Poisson's ratio.[23]

EXPERIMENT

The PVE was 96% 1,2-polybutadiene (obtained from Bridgestone Americas) having a weight average molecular weight=153 000 D. From 0% to 0.666% by weight dicumyl peroxide cross-linker (Varox DCP-R from the R.T. Vanderbilt Co.) was added to cyclohexane solutions of the polymer. After drying, networks were prepared by curing for 30 min at 150 °C. These samples are identical to those of a previous study.[9] The number of monomer units per elastically effective network N was determined from the modulus at mechanical equilibrium with the assumption of affine network behavior (giving an upper limit on N). These values, which are inversely related to the degree of cross-linking, are listed in Table I. Specific volumes were measured as a function of temperature for each sample over a typical range from −5 °C to ca. 80 °C at pressures from 10 to 200 MPa. These experiments were carried out using a Gnomix apparatus,[24] based on the confinement technique using mercury. The apparatus was modified by cooling with thermostated liquid-nitrogen vapor to extend the temperature range below ambient. The dynamic shear modulus G in the glassy state was measured using a Bohlin mechanical spectrometer on cylindrical samples (6.35 mm radius and 6 mm height). Data was obtained isothermally at temperatures from T_g and below. The reported values are for sufficiently low temperatures (at least 15 deg below T_g) that the dependence of G on temperature was negligible. In the glassy state the shear modulus had only a weak frequency dependence over the measured range of 0.01–2 Hz.

RESULTS

Representative PVT data are shown in Fig. 1 for PVE cross-linked with 0.056% and 0.666% peroxide. The liquid thermal-expansion coefficient is smaller for the more highly cross-linked networks (Table I). This weakens the change in slope of the volume data at the glass transition. The temperature of the latter was determined by fitting the equilibrium ($>T_g$) isobaric $V(T)$ data to the Tait equation,[24] with the temperature of the deviation from these fits taken to define $T_g(P)$. The value at ambient pressure was then determined by extrapolation from 10 MPa, the lowest pressure yielding reliable volumes; these results are displayed in Fig. 2. For comparison, the temperatures at which the peak in the dielectric loss occurs at 1 Hz (Ref. 9) are also plotted.

Although there is a systematic decrease in the liquid thermal expansivity with the extent of cross-linking, below T_g this effect is much weaker. The bulk expansivity $B=V^{-1}(dV/dP)|_T$ at the glass transition is almost constant for the networks (Table I). This is in contrast to the shear modulus, which above T_g is directly proportional to the cross-link density.[5] However, in the glassy state, G shows a small but significant decrease with increased cross-linking (Table I). We use the value of $G(T_g)$ as an approximation to its high-frequency limiting value. While this underestimates the latter, it serves as an acceptable measure of the dependence on the degree of cross-linking.

As indicated in Fig. 1, T_g is an increasing function of pressure. The inset to Fig. 2 shows representative results for one of the networks having an intermediate degree of cross-linking. The pressure coefficient of T_g decreases with cross-linking, varying from 243±41 deg/GPa for linear PVE to 152±8 deg/GPa for the tightest network (0.666% dicumyl peroxide).

The relative contribution of volume and temperature to the relaxation times is reflected directly in the ratio of the isochoric and isobaric activation enthalpies. This ratio is usually evaluated from measurements of the relaxation times, either by dielectric or light-scattering spectroscopy, as a function of temperature and pressure. However, E_V/E_P can be obtained using several relations directly from the PVT

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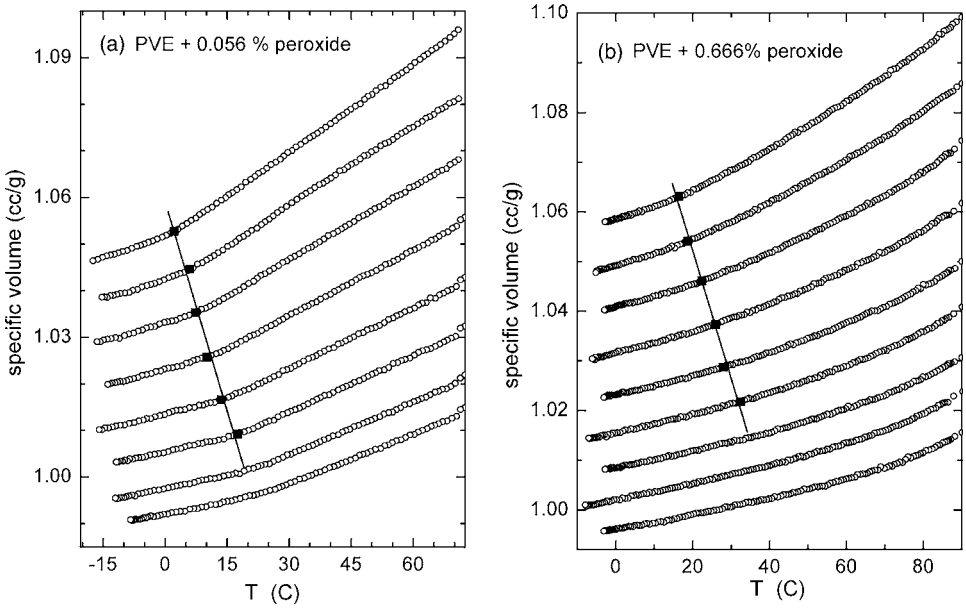

FIG. 1. Specific volume vs temperature for PVE cross-linked with (a) 0.056% and (b) 0.666% peroxide (only a fraction of the data are shown for clarity). The fitted pressures are (from top to bottom in both figures) 10, 30, 50, 75, 100, and 125 MPa. The volume change at T_g for the other isobars [(a) $P=150$ and 170 MPa; (b) $P=150, 175$, and 200MPa] is too small to analyze and the data would not affect the extrapolation to zero pressure. The solid squares correspond to $T_g(P)$; the fitted lines yield the isochoric thermal-expansion coefficient.

data, circumventing the need for relaxation measurements. An equation due to Naoki *et al.*[25] expresses the enthalpy ratio in terms of the product of the isochoric thermal pressure coefficient, $(\partial P/\partial T)_V$ (equal to the ratio of the thermal-expansion coefficient and the bulk compressibility), and the change in temperature with pressure at constant value of the relaxation time, $(\partial T/\partial P)_\tau$. Recognizing that the latter is just the pressure coefficient of T_g[13] (see Fig. 2) gives

$$E_V/E_P = 1 - \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{dT_g}{dP}\right). \tag{1}$$

Alternatively, the isobaric and isochronic expansivities can be used,[26]

$$E_V/E_P = \left(1 - \frac{\alpha_P}{\alpha_\tau}\right)^{-1}. \tag{2}$$

Both equations are evaluated at T_g and ambient pressure using the PVT data for each of the PVE samples. The results are displayed in Fig. 3. There is a systematic increase in E_V/E_P with the degree of cross-linking, reflecting a stronger contribution from thermal energy, relative to that from volume, in governing $\tau_\alpha(T)$. At the highest cross-linking densities, the enthalpy ratio levels off in the same manner as T_g (Fig. 2). This is consistent with a published work indicating that when the network chain length becomes on the order of the length scale associated with the local segmental dynamics, cross-link density dependences level off.[27]

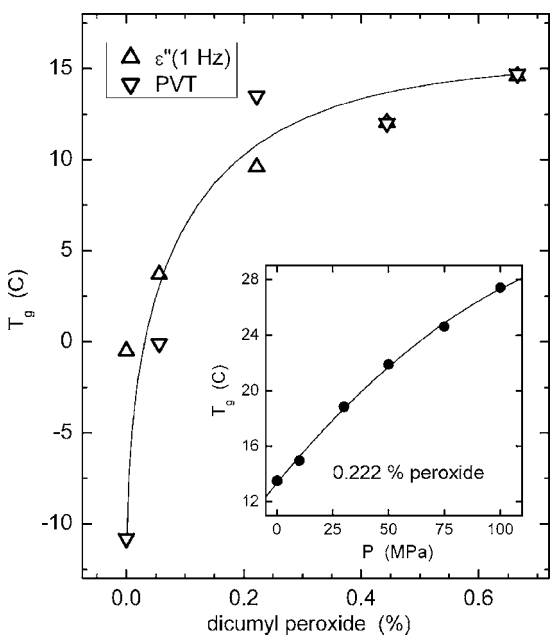

FIG. 2. The (ambient pressure) glass transition temperature determined for the networks from the thermal expansivities, along with the temperature at which the α dispersion in the dielectric loss has a maximum at 1 Hz (from Ref. 9). The solid line is only to guide the eyes. The inset displays the pressure dependence of T_g from the PVT data for PVE cross-linked with 0.222% dicumyl peroxide. The line is a quadratic fit yielding $dT_g/dP = 198 \pm 17$ deg/GPa.

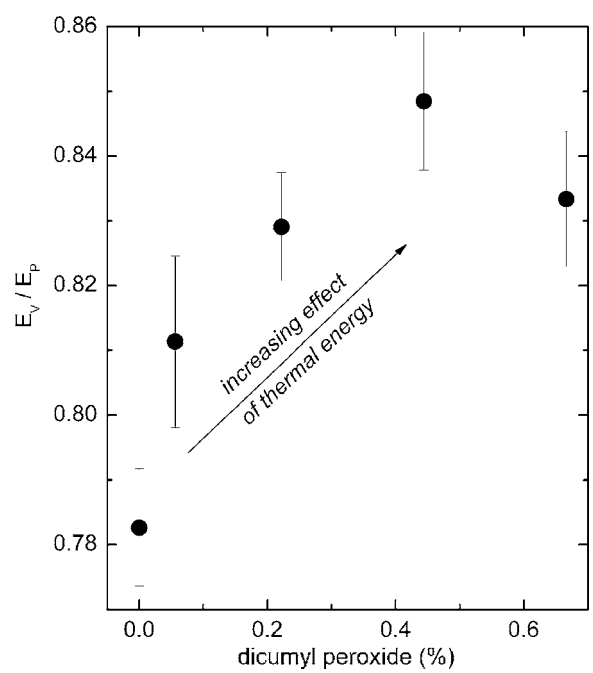

FIG. 3. Ratio of the isochoric and isobaric activation enthalpies determined at T_g for the PVE networks.

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DISCUSSION

The most notable dynamic property associated with glass formation is the divergence of τ_α with decreasing temperature. Thus, models for the glass transition focus on this property, attempting to identify the factors (free volume, thermal energy, and configuration entropy) governing the divergence of τ_α. While these issues remain in debate, an experimental approach, at least, enables the roles of volume and temperature to be quantified. We find herein that the more cross-linked the PVE (that is, the more constraints on the network chains), the less the influence of volume on τ_α. This seems counterintuitive—the confluence of many chains at the high-functionality junctions would seem to require more volume for local motions. However, a somewhat analogous effect is observed for blends of polyphenylene oxide (PPO) and polystyrene (PS).[28] With increasing concentration of the latter, intermolecular constraints are mitigated due to the lower T_g of PS. Nevertheless, the dynamics of blends with higher PS content are less influenced by volume relative to the effect of temperature. The specific volume of the blend is smaller than that of either neat component; however, the importance of volume in determining $\tau_\alpha(T)$ decreases.

The enthalpy ratio E_V/E_P, used to deduce energy and volume effects, is numerically equal to the ratio of the isochoric and isobaric fragilities, defined, respectively, as $m_V \equiv d\log\tau_\alpha/dT_g/T|_{V,T_g}$ and $m_P \equiv d\log\tau_\alpha/dT_g/T|_{P,T_g}$, that is,

$$E_V/E_P = m_V/m_P. \tag{3}$$

The isobaric fragility is the common metric obtained from experiments at atmospheric pressure. The isochoric fragility, however, can be determined only by high-pressure experiments. The isochoric behavior of the relaxation time allows the contribution of T to the relaxation time to be isolated; the isobaric fragility convolutes the dependences of T and V.

Using Eq. (3) and the previously reported m_P for the (equivalent) PVE networks,[9] we calculate the fragility at constant volume. We find that similarly to m_P, m_V increases with the degree of cross-linking. The isochoric fragilities are plotted in Fig. 4 versus m_P. It has been shown that there is a linear correlation between these two quantities; to wit, $m_P = (37\pm3)+(0.84\pm0.05)m_V$.[22] Data for three dozen glass formers are included in Fig. 4, where it can be seen that the PVE networks conform to the general pattern. This relationship between m_P and m_V implies that fragility itself reflects the relative interplay of temperature and density near T_g. From this correlation, larger m_P implies larger ratio of m_V/m_P, i.e., τ becomes more a function T alone. From this correlation we note that the limiting cases of $m_V/m_P=0$ (τ only a function of V) and $m_V/m_P=1$ (τ only a function of T) correspond to the limiting values of the fragility, $m_P=37\pm3$ and $m_P=231\pm72$, respectively.

The increasing fragility of the PVE networks with increasing cross-linking means that the dynamics are more thermally activated, with a weaker influence from "jamming" (hard-core repulsion). The main effect of the cross-links is therefore an increase of the average intermolecular barrier of the chain segments.

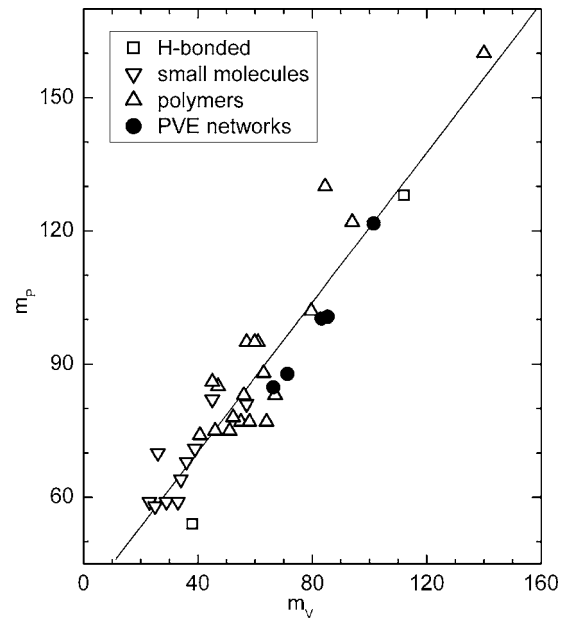

FIG. 4. Isobaric fragility vs isochoric fragility for the PVE networks (filled circles), along with data from Ref. 22 for polymeric and molecular glass formers. Linear regression yields $m_P=(37\pm3)+(0.84\pm0.05)m_V$.

Novikov and co-workers[23,29] have attempted to relate the fast dynamics of glass-forming liquids to their lower frequency properties at T_g and higher temperatures. They have proposed a correlation of fragility with Poisson's ratio, or equivalently with the ratio of the bulk and shear moduli of the glass, $m_P=29(K/G-0.41)$.[23] In Fig. 5 the isobaric fragilities of the PVE networks are plotted versus K/G. Following Ref. 23, we fit a line to the data points (correlation coefficient=0.89, standard deviation=8), obtaining a slope significantly larger than the value found for molecular liquids. Thus, while our data are not inconsistent with the hypothesized relation between m_P and K/G (although the scat-

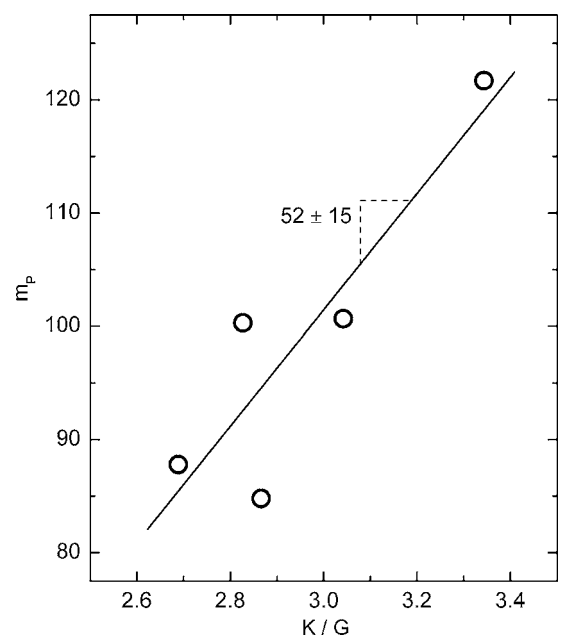

FIG. 5. Isobaric fragility vs the ratio of bulk and shear moduli measured in the glassy state for the PVE networks. The linear fit has the indicated slope.

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ter is substantial both herein and in Refs. 23 and 29), the fragility of the PVE networks changes more strongly with K/G than the "universal behavior" of molecular liquids. Polymers were excluded from the analysis in Ref. 23 because their fragility varies with molecular weight.[30–32] The exceptional behavior of polymers is also seen in the deviations[33,34] from the proposed correlations of fragility with various thermodynamic quantities.[35,36]

SUMMARY

The local segmental relaxation properties of PVE networks were investigated using PVT and mechanical measurements, in combination with previous dielectric relaxation results on equivalent materials. An increasing cross-link density increases the glass transition temperature and the fragility (measured at constant pressure). We find herein that the fragility of the networks measured at constant volume also increases with the degree of cross-linking. This result is consistent with the linear correlation between the isobaric and isochoric fragilities. From PVT measurements through T_g, we find that the relative degree to which segmental relaxation is governed by temperature (thermally activated) as opposed to volume (jamming) increases with cross-link density. Thus, more constraints on the network chains lead to a weaker influence of volume on the dynamics.

In the glassy state, the shear modulus decreases with cross-linking, which is opposite from the behavior in the equilibrium rubber. Since the bulk modulus is essentially invariant to cross-linking, the ratio K/G increases in parallel with the fragility of the networks. This trend is in accord with a relationship between the fast dynamics and the slower relaxations measured near T_g.

ACKNOWLEDGMENT

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Erratum: "Isobaric and isochoric fragilities and the influence of volume on the temperature dependence of local segmental relaxation in polyvinylethylene networks" [J. Chem. Phys. 123, 204905 (2005)]

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In our paper[1] there is an error in the ordinate scale of Fig. 1. The specific volumes are incorrect. The corrected values are in the new figure below. This error does not affect the remaining content of the paper.

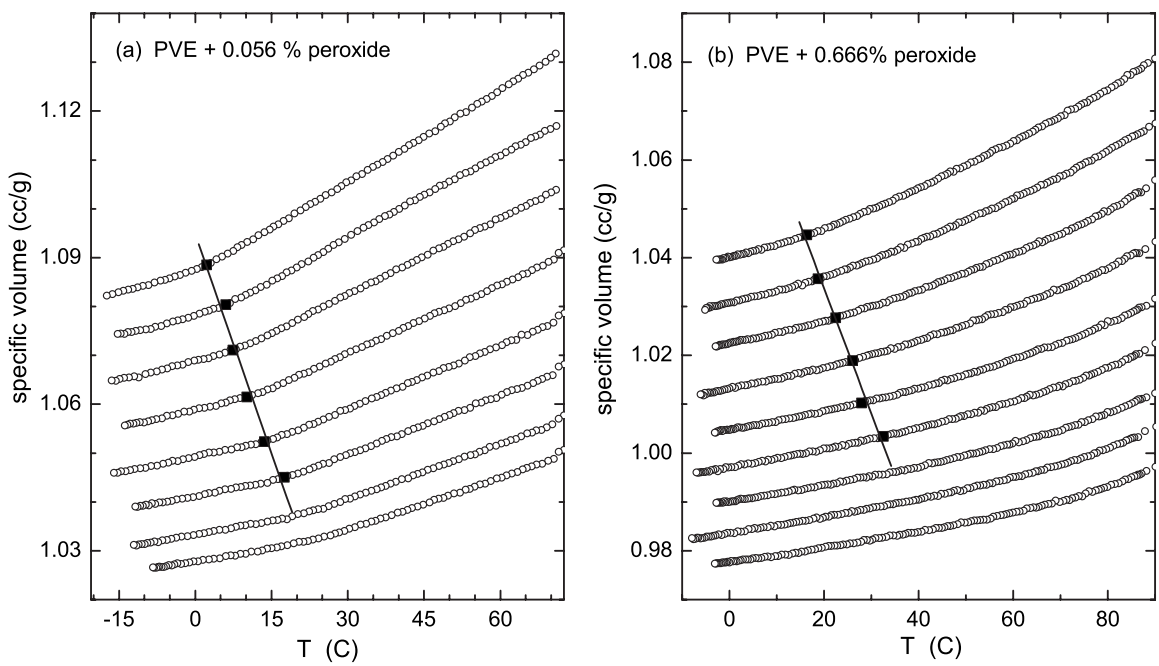

FIG. 1. Specific volume vs temperatures for PVE crosslinked with (a) 0.056 and (b) 0.666% peroxide (only a fraction of the data are shown for clarity). The pressures are (from top to bottom in both figures) 10, 30, 50, 75, 100, and 125 MPa. The solid squares correspond to $T_g(P)$, the fitted lines to which yield the isochoric thermal expansion coefficient.

[1] C. M. Roland, D. F. Roland, J. Wang, and R. Casalini, J. Chem. Phys. **123**, 204905 (2005).

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