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PAPER

Effects of cross-links, pressure and temperature on the thermal properties and glass transition behaviour of polybutadiene

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The thermal conductivity κ , heat capacity per unit volume ρc_p and glass transition behaviour under pressure have been established for medium and high vinyl content polybutadiene PB with molecular weights 2600 and 100 000 and their highly cross-linked (ebonite) states obtained purely by high-pressure high-temperature treatments. Cross-linking eliminates the glass transitions and increases κ by as much as 50% at 295 K and 1 atm, and decreases ρc_p to a limiting level close to that of the glassy state of PB, which is reached before the ultimate cross-link density is achieved. The pressure and temperature behaviours of κ are strongly changed by cross-links, which increases the effect of temperature but decreases the effect of pressure. We attribute these changes to a cross-linked induced permanent densification and consequential increase of phonon velocity simultaneously as conduction along polymer chains is disrupted. The glass transition temperatures for a time scale of 1 s are described to within 0.5 K by: $T_g(p) = 202.5 (1 + 2.94 p)^{0.286}$ and $T_g(p) = 272.3 (1 + 2.57 p)^{0.233}$ (p in GPa and T in K) up to 1 GPa, for PB2600 and PB100000, respectively, and can be estimated for medium and high vinyl content PBs with molecular weights in between by a constant, pressure independent, shift in temperature.

Introduction

Cross-linking of polymer chains is an important method used to impart desirable mechanical properties to polymers. It is commonly achieved with the aid of cross-linking agents, but also other methods are used such as radiation and temperature-pressure treatments, or a combination of these. The connection between cross-linked (network) polymers properties and network characteristics, *e.g.* cross-link density¹ and distribution, crystallization² and dynamics,³ is important knowledge for further development of network polymers and polymer based gels and composites. Despite the long history of network polymers, interesting details about cross-linking processes and the resulting networks are still frequently revealed, partly because of the growing interest in properties of polymer nano-composites and gels. In this context, new methodologies to evaluate cross-link characteristics in pure⁴ and filled⁵ network polymers, as well as computer simulations,⁶ have become important tools to understand effects of a changing network and inclusion of fillers.^{7,8} Besides strongly affecting mechanical properties, cross-linking may also influence the glass transition behaviour^{1,9} as well as other important properties in polymer technology such as the thermal properties,¹⁰ which are the subjects of this study.

Previous high-pressure studies, *e.g.* by Frenkin *et al.*¹¹ and more recently by Kaminski *et al.*,¹² have shown that some polymers can be cross-linked without the use of cross-linking agents by applying high pressure. Thus, it is possible to study the effect of cross-linking on various properties without the influence of cross-linking chemicals. *In situ* investigations of properties are, however, rare. We have recently investigated the use of high-pressure high-temperature treatments to cross-link polyisoprene and shown that a suitable treatment at pressures above 0.5 GPa and temperatures near 500 K gives a densified elastomeric state, or a network polymer.¹³ In the case of polyisoprene, the cross-linking rate was relatively low in the studied high-temperature high-pressure range up to ~ 0.75 GPa and ~ 500 K. In this work, we have investigated polybutadiene PB, which can be cross-linked to significantly higher cross-link densities by treatment under similar conditions. PB is a synthetic polymer, which is attributed to good abrasion resistance, high resilience and heat stability making it very useful in tyre technology. It is easily cross-linked to various degrees of cross-link densities to achieve properties ranging from elastic to hard or ebonite-like. High pressure cross-linking of PB has been previously studied by *ex situ* measurements for pressures up to 0.3 GPa at 513 and 523 K, which gave cross-link densities typical of an elastomer,¹⁴ and above 4 GPa in the 373–453 K range, which gave properties ranging from elastic to brittle.¹⁵ By simultaneous high pressure, *in situ*, measurements it is possible to determine the kinetics of the cross-linking

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process as well as to observe changes in properties, and to study the effect of both temperature and strong isothermal densification on the polymer properties before and after cross-linking. This is a relatively unexplored method to alter the state of a network polymer and obtain denser forms to augment interactions in pure and filled polymers.⁸ We have here investigated two different PBs, with relative molecular masses of 2600 (liquid) and 100 000 (solid), *i.e.* below and well above the entanglement limit of about 3850 for 1,2-PB.¹⁶ This has enabled us to follow the changes in thermal properties as these two PBs are cross-linked into hard ebonite-like network polymers, which reduces the flexibility of the chains simultaneously as the inter-chain interaction increases through covalent bonds and irreversible densification. Both samples had medium or high vinyl content, which promotes cross-linking.

Experimental

Samples of solid polybutadiene (beads, ~29% crystallinity), PB100000, which contained 7% *cis* 1,4 and 93% vinyl 1,2 with an approximate relative molecular mass (molecular weight) M_r of 100 000 (weight average), and phenyl terminated (99 mole % unsaturation) liquid polybutadiene, PB2600, which consisted of 45% vinyl 1,2; 20% of *trans* 1,4 and 35% of *cis* 1,4 with $M_r \approx 2600$ (number average), were both purchased from Scientific Polymer Products, Inc.

The transient hot-wire method was used for measuring the thermal conductivity κ and the heat capacity per unit volume ρc_p , where c_p is the isobaric specific heat capacity and ρ is the mass density.¹⁷ The probes used were Ni wires of ~40 mm length and 0.1 mm diameter. In order to best use the limited space available in the high-pressure vessel, the wire is placed horizontally in a ring of constant radius configuration within the sample cell made of Teflon. To determine κ and ρc_p , the hot-wire probe embedded in the sample (PB) was electrically heated by a 1.4 s pulse, yielding a temperature rise of about 3.5 K (corresponding to a transient heating rate of 150 K min⁻¹), *i.e.* the hot-wire works as both heater and sensor for the temperature rise and the latter is calculated using the wire's electrical resistance-temperature relation. The values for κ and ρc_p are obtained through a fit of the analytical solution of the temperature rise of an infinitely long, infinitely conducting wire immersed in an infinitely large specimen.¹⁸ The inaccuracy is estimated as 2% in κ and 5% in ρc_p . The standard deviation in the measurements is an order of magnitude smaller than the inaccuracy.

The method is well-suited to establish the glass transition behaviour under pressure as ρc_p shows the typical sigmoid-shaped increase of c_p and the temperature dependence of κ generally changes due to the increase in the thermal expansion coefficient.¹⁹ In addition, two anomalies may arise in the form of a peak in κ and a dip in ρc_p when the relaxation time of a relaxation process is of order of the probe time, *i.e.* 1 s.^{20,21} In the study here, such are observed and due to the segmental relaxation of PB.

Two different piston-cylinder type apparatuses of 45 mm internal diameter, which can operate up to 1 and 2 GPa, were used during the investigations of the liquid and solid PB, respectively. A general description of a piston-cylinder vessel

and a sample cell has been given previously.²² The pressure p was determined from load/area, with an empirical correction for friction, which had been established using the pressure dependence of a manganin wire. The maximum inaccuracy in pressure was estimated as 40 MPa at 1 GPa.

The temperature of the sample was controlled *via* the power of an electrical resistance heater placed on the vessel, and could thereby be kept constant by a PID control system during isothermal measurements. For measurements below room temperature, the vessel was cooled using liquid nitrogen. The sample temperature was measured using an internal Chromel Alumel thermocouple, which had been calibrated against a commercially calibrated diode sensor with an accuracy of 10 mK. The pressure fluctuation during isobaric measurements and the cross-linking experiments, which was also controlled using a PID-controller, was less than 1 MPa.

A Renishaw 1000 grating spectrometer, in backscattering geometry, equipped with an argon ion laser (514 nm) was used for Raman analysis of the untreated and cross-linked samples in the range 3800 to 250 cm⁻¹.

The samples were swelled in *n*-heptane at room temperature for 24 h and the cross-link densities were calculated by the Flory-Rehner equation,^{23,24} through a procedure previously described in detail.^{13,25} The polymer-solvent interaction parameter χ was calculated from $\chi = 0.37 + 0.52\phi^{14}$ where ϕ is the PB volume fraction in the swelled sample. Mass density was measured by the Archimedes' principle by immersing in water.

Results and discussion

High-pressure high-temperature cross-linking of PB and the effect on thermal properties

The thermal properties and glass transition temperature T_g of PB2600 and PB100000 were first established by isothermal and isobaric measurements at temperatures below ~400 K. Subsequently, the samples were cross-linked by high-pressure high-temperature HP&HT treatment at 0.5 and 1.0 GPa (PB2600), and 1.5 GPa (PB100000) near 500 K, and the changes in the thermal properties monitored, *in situ*. The cross-link densities of the recovered samples were determined by the swelling method. The HP&HT treatment changed the samples from liquid (PB2600) or relatively soft solid (PB100000) in the as-purchased, or untreated, states²⁶ to hard, ebonite-like, states after cross-linking. Besides the swelling results, the samples were characterized by Raman and X-ray diffraction measurements.

It is established that the chemical structure of PBs can be analysed by Raman spectroscopy using the C=C stretching peaks of vinyl, *cis* and *trans* configurations at 1640, 1650 and 1664 cm⁻¹, respectively.^{27,28} In this range, the Raman spectrum of PB2600 shows the strongest peak at 1641 cm⁻¹ (Fig. 1), but also significant peaks at 1655 and 1668 cm⁻¹, which confirm a relatively high vinyl content as well as significant contents of *cis* and *trans* configurations. The PB100000 spectrum shows only one distinct peak at 1633 cm⁻¹, which indicates that the sample has almost 100% vinyl content (93% vinyl and 7% *cis*). As shown in Fig. 1, the HP&HT treatments caused significant changes of the Raman peaks, in particular for those

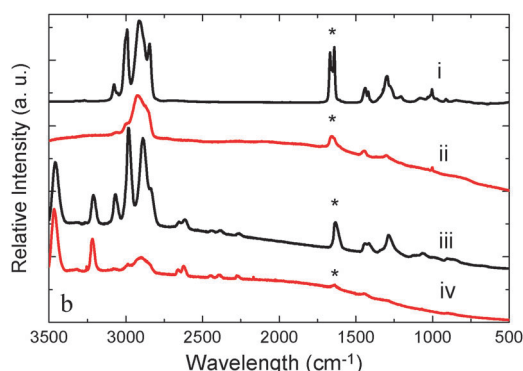


Fig. 1 Raman spectra of polybutadiene: (i) untreated PB2600 and (ii) PB2600 treated at 1 GPa and 513 K during 1 h; (iii) untreated PB100000 and (iv) PB100000 treated at 1.5 GPa and 513 K during 5 h. Asterisks denote the C=C stretching vibration peaks.

associated with the C=C double bond. The peaks due to C=C stretching in PB2600 have merged into one broad weak peak centred at $\sim 1650\text{ cm}^{-1}$, and the peak at 1633 cm^{-1} for PB100000 has almost vanished. Moreover, the peaks near 3000 cm^{-1} , which are assigned to the symmetric and asymmetric vibrations of CH=CH (*cis* and *trans*) and CH₂=CH (vinyl),²⁷ have also become weaker and merged into a single broad peak. These changes corroborate previous results that a significant number of the vinyl double bonds are consumed by radicals in neighbouring chains to form cross-links during the HP&HT treatment.¹⁴ X-Ray results before and after the treatment showed that the slight degree of crystallinity of PB100000 had decreased further by the treatment (spectra not shown).

The samples were subjected to various HP&HT treatments and one sample of PB2600 was annealed during 4.5 h at 500 K and 0.5 GPa. This gave a relatively high cross-link density ν of

$(6.5 \pm 0.4) \times 10^{-4}\text{ mol cm}^{-3}$ in the final state, but still κ and ρc_p remained constant to within the imprecision of the method ($\sim 0.2\%$) during the cross-linking process. However, the recovered sample at 1 atm and 295 K had about 8% higher κ compared to the untreated sample, *i.e.* the changes in the thermal properties due to cross-linking depend on the temperature–pressure T – p conditions and are most significant near 1 atm. In a second cross-linking experiment, a new sample of PB2600 was annealed at 1 GPa and 513 K during 1 h. In this case, κ increased 2% simultaneously as ρc_p decreased 4% in a time dependent manner. Fits using exponential functions of the type $\exp(-t/\tau)$, where t is time and τ is the time constant, yielded the time constants 10 min and 37 min for $\rho c_p(t)$ and $\kappa(t)$, respectively. When the temperature was decreased and the pressure reduced to 295 K and 1 bar, the difference in κ compared with the untreated sample increased to as much as 48%. The corresponding decrease in ρc_p was 15%. The subsequent analysis of the cross-link density gave $\nu = (2.0 \pm 0.3) \times 10^{-3}\text{ mol cm}^{-3}$.

Cross-linking of PB100000 was studied in two different experiments at 1.5 GPa (Fig. 2). In one case, it was done on continuous heating at $\sim 0.5\text{ K min}^{-1}$ rate up to 522 K, followed by annealing for 6 h at $522 \pm 2\text{ K}$. As shown in Fig. 2 (panels a and b), the results show a glass transition at 395 K before cross-linking becomes noticeable at 482 K, which is reflected by a rather abrupt 6% increase in κ and 8% decrease in ρc_p in the 482 K to 520 K range. At 520 K, the time-dependent decrease in ρc_p ceased whereas κ continued to increase slowly with time. In the subsequent annealing experiment at $\sim 522\text{ K}$ (Fig. 2d), κ increased further by about 6%, which gave a total cross-linked induced increase of 12%. The time-dependent increase occurred in a sluggish process that had a time constant of 3.5 h. As for PB2600, the difference in κ

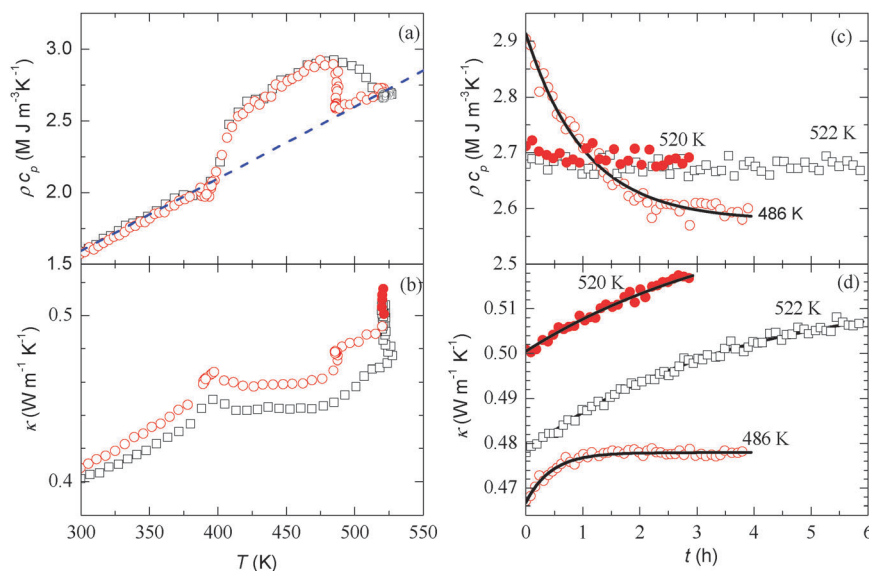


Fig. 2 (a) Heat capacity per unit volume and (b) thermal conductivity of PB100000 plotted against temperature at 1.5 GPa: (□) heating at 0.5 K min^{-1} rate up to $\sim 522\text{ K}$ where the sample was annealed (panels c and d), and (○) data for a new sample heated to 486 K, where it was annealed for 4 h, further heated to 520 K and (●) annealed for additional 4 h. The dashed line represents a linear extrapolation for ρc_p of the glassy state. (c) Heat capacity per unit volume and (d) thermal conductivity of PB100000 plotted against time during annealing at 1.5 GPa and: (○) 486 K, (●) 520 K, (□) 522 K. The solid curves represent fitted functions.

compared to the untreated sample increased at decreasing pressure and became 35% near 1 atm and 295 K. In this case, the cross-link density of the final state was too high for measurements using the swelling method. On the basis of the resolution in our experiment using the swelling method, we estimate that the cross-link density was higher than $\sim 7 \times 10^{-3} \text{ mol cm}^{-3}$.

In the second experiment at 1.5 GPa, a new sample of PB100000 was first heated up and annealed for 4 h at 486 K (Fig. 2), with a 2% increase of κ , then heated to 522 K which raised κ by 3%, and finally annealed for 4 h at 520 K with an additional 6% increase of κ , *i.e.* essentially the same total increase as in the first experiment (12% and 11% in the first and second experiment, respectively). The corresponding decreases of ρc_p during the 4 h anneals at 486 and 520 K were 10% and 0%, respectively. Moreover, the time constants for the changes in κ (and ρc_p) were 0.5 h (and 1 h) at 486 K, and ~ 4 h at 520 K. Thus, both experiments at 1.5 GPa show qualitatively the same results: ρc_p decreases as more cross-links are formed, but the decrease levels off well before reaching the ultimate cross-link density. The latter is deduced from the continued increase of κ with time, which is confidently attributed to a growing number of cross-links. We also note that the changes due to cross-linking occur in a time-dependent manner that differs between $\kappa(t)$ and $\rho c_p(t)$.

We can conclude that despite the differences in molecular weight and vinyl content, the behaviours of the two samples, PB100000 and PB2600, are similar, *i.e.* the process transforms the samples into highly cross-linked, ebonite-like, states with similar changes in the thermal properties. Thus, although the effects of the differences in *e.g.* chemical structure and molecular weight are convoluted, the results imply that the differences do not strongly affect the resulting cross-link densities and thermal properties. In order to understand the origin of the characteristic changes in the thermal properties caused by the cross-linking process, and the similar results for PB100000 and PB2600, we turn to theory for κ and $(\rho)c_p$.

The heat capacity of the glassy state of a polymer is mainly due to (skeletal) vibrations,²⁹ and on heating to above the glass transition, configurational contributions in the form of segmental and normal motions of the polymer chains, possibly together with an increase of the vibrational c_p , raise c_p in a sigmoid-shaped manner at T_g . (Recently, arguments and results have been put forward in favour³⁰ and against^{31,32} significant changes in the vibrational part of c_p .)

As shown by the linear extrapolation of the heat capacity of the glassy state, *i.e.* the vibrational part of c_p corresponding to the frozen state (dashed line in Fig. 2a), the cross-linking process gradually transforms PB100000 to a state with a heat capacity close to that predicted for the glassy state under the same conditions. (The results on cooling after cross-linking agreed to within 0.5% with those of the glassy state just below T_g .) This means that the configurational contributions diminish and eventually vanish as the cross-link density increases. In the first part of the cross-linking process, the stiffening of the structure shifts T_g to higher temperatures,¹³ and finally PB transforms into a glassy state heat-capacity-wise, and the changes in c_p cease. However, although a further increase of the cross-link density does not affect c_p , κ continues to increase

with time. That is, further stiffening of the structure promotes phonon heat transport whereas the phonon heat capacity per unit volume is unaffected and equal to that of the glassy counterpart of the liquid state. This shows that the configurational freedoms have already ceased and that the vibrational part of c_p is relatively unaffected by further increase of cross-links.³³ The reason for the promoted heat transport can be understood in terms of theory for κ .

On the basis of the Debye model, κ is given by³⁴

$$\kappa = \frac{1}{3} \rho c v \ell, \quad (1)$$

where v is the phonon velocity, ℓ is the phonon mean free path and ρc is the heat capacity per unit volume of the heat-carrying phonons. The changes in these parameters can be predicted based on previous knowledge and thermodynamic relations. Since the cross-linking process is promoted by pressure, it suggests that the cross-linked state has a smaller volume than the state without cross-links, which was also corroborated by measurements of the density. These showed that the density of PB100000 increased $\sim 14\%$, from 0.91 g cm^{-3} for the untreated sample to 1.04 g cm^{-3} for the 1.5 GPa treated sample recovered at 1 atm and 295 K. (Since the highly cross-linked state becomes less compressible, this difference would be smaller at 1.5 GPa.) The heat capacity, however, must decrease due to the reduced flexibility caused by the cross-links, which is also verified by the measured decrease of the (total) heat capacity per unit volume. Concerning the phonon mean free path, we note that the heat transport along a chain is significantly higher than that perpendicular to a chain. This was recently studied by stretching lightly cross-linked PB, which aligns the chains giving up to 25% higher thermal diffusivity κ along the predominant alignment (stretch) direction compared to that in the perpendicular direction.¹⁰ Cross-links should induce changes in the strain field for propagation of phonons which cause phonon scattering and a decrease of ℓ along the chains, but the overall ℓ would decrease only slightly due to the already short ℓ in predominantly amorphous polymers like PB. Considering these changes in the parameters of eqn (1), it follows that the cross-linked induced stiffening of the structure and densification increases κ primarily through an increase of the phonon velocity. This effect apparently promotes κ even at already high cross-link densities where the change in ρc_p diminishes. The cross-linked induced change in κ appears qualitatively similar to that caused by an isothermal pressure increase, which normally also increases the phonon velocity, whereas the other parameters of an amorphous state are less affected.

Effects of pressure and temperature on the thermal conductivity and heat capacity per unit volume

Fig. 3 shows the effect of pressure on ρc_p and κ in PB2600 and PB100000 and their cross-linked counterparts. As shown, ρc_p (panels a and c) of the cross-linked samples is essentially independent of pressure and no glass transition induced changes are visible. Due to the hardness of the samples, the compressibility must be small, *i.e.* the density does not increase much and the small increase is compensated by a small decrease in the heat capacity. The small change in ρc_p with

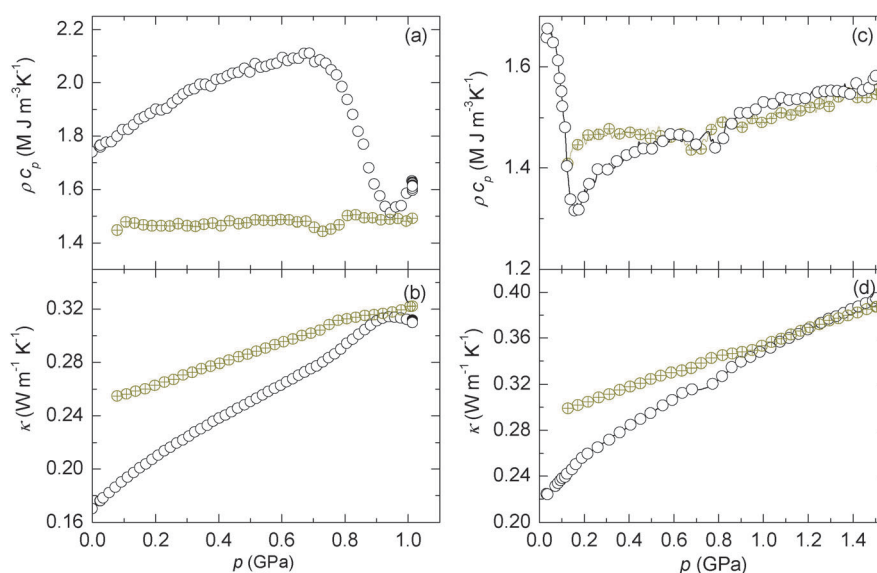


Fig. 3 (a) Heat capacity per unit volume and (b) thermal conductivity as a function of increasing pressure at 294 K for PB2600: (○) untreated, (⊕) cross-linked by treatment for 4 h at 1 GPa and 513 K. (c) Heat capacity per unit volume and (d) thermal conductivity as a function of increasing pressure at 295 K for PB100000: (○) untreated, (⊕) cross-linked at 1.5 GPa according to the procedure described in Fig. 2.

pressure is an effect of the high degree of cross-linking and it is probably augmented by the densified conditions under which the process is conducted. The change of ρc_p for the untreated samples is larger due to the significantly stronger densification, and the glass transitions give strong decreases in the heat capacities at about 0.75 and 0.05 GPa for PB2600 and PB100000, respectively.

As shown in Fig. 3, there is also a striking difference in κ (panels b and d) between the treated and untreated samples, where the latter show significantly stronger pressure dependence of κ . The difference in κ between the untreated and cross-linked states is large near 1 atm but diminishes with increasing pressure and the states have almost the same κ near the pressure of the cross-linking processes. The main change in κ caused by the pressure induced densification is due to the raise in the phonon velocity. It has been shown that the longitudinal sound velocity of typical elastomers increases by about a factor of 2 (1.7, 1.7 and 2.5, respectively, for three different elastomers) on pressurization up to 1 GPa at room temperature,³⁵ which is somewhat larger than the corresponding increase in κ of the untreated PB2600 (1.8) and PB100000 (1.6). Thus, the change in velocity can account for all the change in κ , whereas the other parameters in eqn (1), viz. ρc of the heat carrying phonons and ℓ , should remain constant or change only to a small extent. The phonon velocity in the cross-linked sample apparently changes relatively weakly with pressure, which we attribute to its ebonite-like state, and therefore it remains high even at low pressures. Thus the effect of increasing pressure on the untreated sample is similar to the effect of cross-linking, which also promotes the phonon velocity.

Fig. 4 shows the temperature behavior of the thermal properties, which has also changed significantly after cross-linking.³⁶ As opposed to the pressure dependence, $\kappa(T)$ of the cross-linked states shows an overall stronger dependence than those of the untreated states. This leads to increasing

difference in κ with increasing temperature. Especially at low pressure and above T_g , κ of the untreated samples decreases on the temperature increase, whereas the temperature dependence for κ of the cross-linked sample remains largely unaffected and κ continues to increase at the highest temperatures. In the low temperature range below about 150 K, decrease of temperature causes a more rapid decrease of κ than for the untreated samples. Comparison between the two isobars at low and high pressure also reveals that pressure influences strongly the behavior for the untreated sample but much less for the cross-linked sample, in correspondence with the isothermal results of κ . In the most extreme case, $\kappa(T)$ of PB100000 of the untreated state at 1.5 GPa becomes higher than that of the cross-linked state at low temperatures. This is remarkable but we can hypothesize about the reason in terms of eqn (1). At high pressures, the difference in phonon velocity between the cross-linked state and the untreated state diminishes. Moreover, although phonon–phonon scattering is not dominant in amorphous polymers it should contribute to thermal resistivity and decrease the phonon mean free path, but phonon–phonon processes diminish on cooling. As a consequence, the relative importance of a cross-linked induced disruption of the heat transport increases and these cross-links act as phonon scattering sources, possibly in the same manner as point defects or larger defects caused by the cross-linked induced changes in the local strain. In particular, these should decrease ℓ and limit the heat transport along the chains of PB100000. A consequence of such scattering, which does not diminish on cooling as much as phonon–phonon scattering, is a drop-off of κ . It occurs when the heat capacity decreases and is not compensated by an increase in ℓ , and it would therefore be more abrupt in the cross-linked samples than in the untreated samples.

We also note that the long chains and crystallinity ($\sim 29\%$) of PB100000 only slightly promote κ , and make it 24% and 14% higher than that of PB2600 at 295 K and 190 K (below the glass transition), respectively. A significant part of

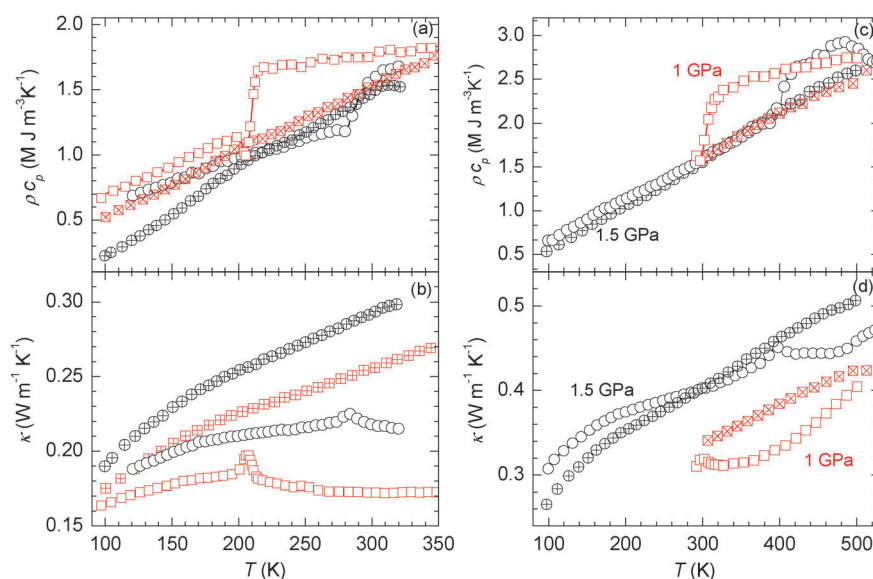


Fig. 4 (a, c) Heat capacity per unit volume and (b, d) thermal conductivity plotted against temperature for: (squares) PB2600, and (circles) PB100000. Filled symbols represent results for cross-linked samples. Panels a and b show results measured at 0.02 GPa (PB2600) and 0.05 GPa (PB100000) but extrapolated to 1 atm, and panels c and d show results at 1 and 1.5 GPa, as indicated. (At 1 GPa, measurements were done only above room temperature.)

the additional difference of about 10% above the glass transition is mostly an effect of the increasing difference in density between PB2600 and PB100000, which arises in the temperature range of ~ 70 K between their glass transitions. Based on previous findings of the effect of chain alignment,¹⁰ we can conclude that the difference in κ of PB2600 and PB100000, caused by the different chains lengths, would be larger if the chains were aligned and not as in this case in a predominantly amorphous state, *i.e.* randomly arranged. However, as shown in Fig. 4b, the slight crystallinity of the untreated PB100000 does not significantly affect the temperature dependence of κ , which is revealed by the almost identical low temperature drop-off of κ as that shown by the fully amorphous PB2600 sample. This is likely due to the random orientation of the (small-sized) lamellae in a mostly amorphous matrix.

Effects of pressure and cross-linking on the glass transition behavior

Isobaric results for κ and ρc_p of PB100000 and PB2600 and their cross-linked counterparts, shown in Fig. 4, also provide data for the reversible pressure effect on the glass transition temperature T_g . To determine $T_g(p)$, the samples were kept below ~ 400 K during isobaric measurements, which avoids (irreversible) cross-linking. The sigmoid-shaped increase in the data for ρc_p shows T_g for a time-scale of 1 s used in the hot-wire method. Moreover, the glass transition also induces an anomalous peak in κ and a dip in ρc_p ,²¹ which occurs at a temperature just below the sigmoid shaped c_p rise attributed to the additional contribution by mainly the configurational modes. The pressure induced densification of the samples shifts T_g to higher temperatures, which is well-described by the empirical expression:³⁷

$$T_g(p) = T_0 \left(1 + \frac{b}{a} p \right)^{1/b} \quad (2)$$

where a , b and T_0 are fitting parameters, and p is the pressure in GPa. The fits yielded $T_0 = 202.5$ K, $a = 1.19$ GPa and $b = 3.50$ for PB2600, and $T_0 = 272.3$ K, $a = 1.67$ GPa and $b = 4.30$ for PB100000.

The fits of eqn (2) are represented by solid lines in Fig. 5 and provide descriptions to within 0.5 K. The $T_g(p)$ for the two samples differs by approximately a constant temperature difference despite the significant difference in molecular weight. It is reasonable to assume that medium and high vinyl PBs with molecular weights in between PB2600 and PB100000 would show identical behavior and, thus, that their $T_g(p)$ is described well by eqn (2) using the parameters of PB2600 (or PB100000) and simply adding the difference in T_g at 1 atm. This estimate gives a maximum error of ~ 4 K at 1.5 GPa for PB100000, and even better agreement is expected for lower molecular weight PB. Roland *et al.*³⁸ have studied dielectric

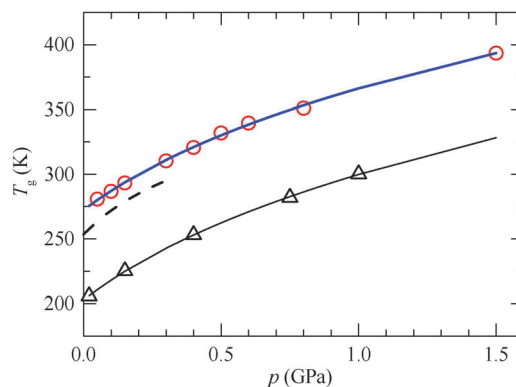


Fig. 5 Glass transition temperature for a time scale of 1 s plotted against pressure for the untreated samples: (Δ) PB2600 and ($\circ$) PB100000. The solid lines represent fits of eqn (2). The dashed line represents values for T_g of PB3000,³⁸ which were also measured on a time scale of 1 s.

relaxation of 1,2-PB (88% vinyl content) with molecular weight 3000 in the pressure range up to 0.3 GPa, and their data for T_g for a time scale of 1 s are described to within ± 1.5 K by a constant shift in T_g for PB2600 (Fig. 5).

With increasing cross-link densities, the glass transition is shifted to higher temperatures and occurs in a wider temperature range,¹³ but for the high cross-link densities achieved here, the results show that the glass transition is eliminated. That is, the cross-linked PB100000 and PB2600 remained in a glassy, ebonite-like, state throughout the temperature range, and would probably remain so up to onset of decomposition.

Conclusions

Treatment of low molecular weight (PB2600) and high molecular weight (PB100000) polybutadienes at temperatures near 500 K in the range 0.5 to 1.5 GPa induces cross-linking and changes the states to hard densified ebonite-like states. This process occurs in a sluggish time dependent manner, with a time constant of 0.5 h at 486 K and 1.5 GPa, and reduces the heat capacity to that of the glassy state. Concurrently, the thermal conductivity increases and becomes as much as 50% higher in the recovered high-pressure treated state of PB2600 than in its untreated state at room temperature. Moreover, the thermal conductivity of the highly cross-linked ebonite states shows stronger changes with temperature, but weaker changes with pressure than the untreated states. We attribute these effects of cross-linking to disruption of the heat transport along the polymer chains and irreversible densification, which raises the phonon velocity in the same manner as densification does on pressurization. We deduce that phonon scattering due to cross-links causes a more rapid drop-off of the thermal conductivity when the temperature is lowered and that the irreversible densification increases the bulk modulus, which reduces the change in density with change in pressure.

PB100000 has ~ 70 K higher glass transition temperature T_g than the liquid PB2600 independent of pressure. Both PB100000 and PB2600 show an initially strong increase of T_g with pressure, which levels off at high pressure. Despite the significant difference in molecular weight and the strong variations with pressure, the shift in T_g stays about constant in the 1 GPa pressure range studied here, which increases the density by about 20%. This common behaviour suggests that the glass transitions of medium and high vinyl polybutadienes with molecular weights in between PB2600 and PB100000 would follow the same dependence on pressure, and that their glass transition at high pressure can be estimated using the difference from that of PB2600 or PB100000 at 1 atm. The high degree of cross-linking achieved during the high-pressure high-temperature treatment eliminates the glass transitions that occur at 202.5 K and 272.3 K on a time scale of 1 s at 1 atm for untreated PB2600 and PB100000, respectively.

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