electrolytes, the nonelectrostatic part of ΔH_t exceeding the electrostatic part by an order of magnitude.[12]

The structural contribution $\Delta H_t^0(\mathrm{st})$ reflects specific solute-solvent interactions that are characterized by partial dehydration followed by partial dioxanation of the ions participating in the process of transferring solute from an aqueous solution to a dioxane-water mixture. Simultaneously the transfer of solute is accompanied by order-creating and order-destroying processes in the two solvents. It is well-known that the dioxane-water mixtures are less ordered than pure water and that the extent of order decreases with increasing proportion of dioxane in the mixture.[7,12,13] Furthermore, evidence exists that the large poly(styrenesufonate) anion is a structure breaker,[14] so that we may consider the alkali-metal poly(styrenesulfonates) as net structure breakers in water and in dioxane-water mixtures. Therefore, more energy must be absorbed when these polyelectrolytes are incorporated into water than when they are disolved in a mixture of dioxane and water. The enthalpy of transfer of poly(styrenesufonates) from water to this binary solvent is thus expected to be exothermic, and its absolute value should increase with the increasing content of dioxane in the mixture. The experimental observations seem to confirm such explanations.

Figure 1 shows that the enthalpy of transfer does not depend on the nature of counterions, indicating that it is primarily determined by the large, highly charged polyion. This experimental observation agrees with the recent refractometric measurements from this laboratory, which show a very similar preferential solvation of various poly(styrenesulfonates) in the binary solvent of water and dioxane.

Acknowledgment. The financial support of the Research Community of Slovenia is gratefully acknowledged.

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Effect of Entropy of Melting on Strain-Induced Crystallization

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ABSTRACT: The seemingly conflicting requirements of enhancing strain crystallization and of hampering temperature-induced crystallization can be satisfied by polymers with a low melting entropy per statistical segment. This condition is met if the entropy in the crystalline state is large. It is remarkable that this happens both with natural rubber (i.e., *cis*-1,4-polyisoprene) and with the butadiene-piperylene copolymers, due to the conformational disorder affecting the chains in spite of their parallel packing, as suggested by Corradini (*J. Polym. Sci., Polym. Symp.* **1975**, *No. 50*, 327).

Introduction

The relevance of strain-induced crystallization of stereoregular polymers to their mechanical properties is generally well recognized. It takes place during fiber spinning, film extrusion, and rubber milling, e.g., improving the processibility of the products. Also, rubberlike networks crystallize when subjected to large deformations, to advantage of their mechanical properties. It appears therefore quite reasonable that the phenomenon has been the object of a large body of experimental and theoretical studies.

Polymer networks, and particularly natural rubber networks, have usually been preferred as models for strain crystallization in view of their ability to approach thermodynamic equilibrium under well-defined conditions,[1] unlike polymer melts or solutions. The aim of the present work is to discuss some of the factors controlling crystallization of a rubber network, with a specific emphasis on the effect of the entropy of melting (s_f). As we shall see, the basic conclusion is that a small value of s_f is favorable to rubber performance, in contrast with some suggestions that it should rather be large.[2]

We shall consider separately the cases of *strain-induced* and of *temperature-induced* crystallization. As for the first item, although Flory's classical theory[1] would be quite adequate for the above-defined purpose, we shall use as a starting point the extension of that theory due to one of us, wherein the angular distribution of crystallinity in a stretched sample is obtained.[3] Our only reason for choosing the latter approach is that it appears better suited for examining the thermodynamic implications of the change undergone by the network during crystallization. In fact, let us recall that the partition function of the elastic network may be factorized into two terms: one embodies the overall elastic energy of the chains regarded as independent objects, while the other depends on the network topology and is usually neglected as being strain-invariant (see, e.g., ref 4, eq 29 and 30). However, in the particular case wherein the strain induces chain crystallization, the topology of the (amorphous) network does change. To the

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0024-9297/83/2216-1167$01.50/0

best of our knowledge the related effect has never been explicitly considered and, although it appears to be small for most practical purposes (as we shall see), we believe it useful to assess its relative importance in general terms. As for the temperature-induced crystallization, we did not carry out any similar investigation, limiting ourselves to results previously obtained by other authors.[5,6]

Thermodynamic Results

(a) Strain-Induced Crystallization. Both Flory's classical paper[1] and the subsequent extension previously referred to[3] are based on the following assumptions: (i) the temperature T is above $T_m°$, i.e., the ideal melting point of the un-cross-linked polymer, the sample is at thermodynamic equilibrium, and chain folding is disregarded; (ii) the chains (i.e., chain sequences connecting different junctions) are sufficiently long and far from complete elongation as to conform to Gaussian behavior, and, in addition, they all have the same length; (iii) conditions of incipient crystallization are investigated (i.e., the crystallized fraction of any chain is much smaller than unity); (iv) the average location of the junctions is affinely displaced upon sample deformation. Besides, while Flory assumes the crystallized stems to be oriented parallel to the stretching direction, they are taken as parallel to the average end-to-end chain vector in ref 3, wherein restrictions in junction fluctuations to account for chain packing[4] are also considered. We shall investigate first the network effect produced by the shortening of the amorphous parts of the chains upon crystallization.

Network connectivity enters the configurational partition function as a factor[4,7]

$$\mathrm{CF} = K\cdot(\det \mathbf{C})^{-3/2} \tag{1}$$

$$\mathbf{C} = \|C_{ij}\| = \|c_{ij}/N_{ij}\| \tag{1'}$$

where i and j are junction indices, c_{ij} is either 1 or 0, depending on whether the two junctions are connected or not, N_{ij} is the number of statistical segments in the connecting chain, and K is an uninteresting constant factor. Apart from the sign, the general term of the determinant may be written as

$$t(i_1 i_2 ... i_n) = (N_{i_1 i_2} N_{i_2 i_3} ... N_{i_{n-1} i_n} N_{i_n i_1})^{-1} \tag{2}$$

where $(i_1 i_2 ... i_n)$ corresponds to any ensemble of closed circuits with k edges, fulfilling the relationship $\sum k = n$ (i.e., the total number of network junctions). When the chains are partly crystallized, N_{ij} is equal to the number of amorphous segments; i.e.

$$N_{ij} = N(1 - w_{ij}) \tag{3}$$

N and w_{ij} respectively being the (uniform) number of chain segments in the network and the crystallized fraction of the chain. Since n is very large and $w_{ij} \ll 1$, $t(i_1 i_2 ... i_n)$ is reasonably well approximated by its geometric average, $\langle N_{ij}\rangle^{-n}$, where $\langle N_{ij}\rangle$ in turn is the geometric average of all the N_{ij}'s. Indicating with f the uniform functionality of the junctions and with k the index of the general chain, the total number of which is $nf/2$, we get

$$\langle N_{ij}\rangle = N \prod_{k=1}^{nf/2} (1 - w_k)^{2/nf} \tag{4}$$

so that eq 2 reduces to

$$t(i_1 i_2 ... i_n) \simeq N^{-n} \prod_{k=1}^{nf/2} (1 - w_k)^{-2/f} \tag{5}$$

From this result, labeling as $\mathbf{C}_0$ the $\mathbf{C}$ matrix in the absence of crystallization, we have

$$\det \mathbf{C} \simeq \det \mathbf{C}_0 \prod_{k=1}^{nf/2} (1 - w_k)^{-2/f} \tag{6}$$

and the free energy contribution $\Delta A = -k_B T \ln (\mathrm{CF})$ is (see eq 1)

$$\Delta A = \Delta A_0 - 3k_B T/f \sum_{k=1}^{nf/2} \ln (1 - w_k) \tag{7}$$

Thus, the crystallization-dependent free energy term for the kth chain, arising from network connectivity, is $-(3k_B T/f) \ln (1 - w_k)$. This result enables us to maintain the same formal viewpoint adopted in ref 3 (i.e., minimization of the free energy is imposed separately for the different chains); we get

$$w(\lambda,T) = 1 - 1/[Nf(1 - \epsilon(T))] - \left\{1/[Nf(1 - \epsilon(T))]^2 + \left(1 - 2\lambda\left(\frac{8}{3\pi N}\right)^{1/2} + \lambda^2/N\right)/(1 - \epsilon(T))\right\}^{1/2} \tag{8}$$

where

$$\epsilon(T) = s_f(T - T_m°)/(^3\!/_2 k_B T) = (2s_f/3k_B)(1 - T_m°/T) \tag{8'}$$

and λ is the elongational ratio *relative to the chain under consideration*. From eq 8 and 8′, the chain melting temperature (i.e., at which $w = 0$) is

$$T_m = T_m°/\left[1 - \frac{3k_B}{2s_f}\left(2\left(\frac{8}{3\pi N}\right)^{1/2}\lambda - \frac{1}{N}\left(\lambda^2 + \frac{2}{f}\right)\right)\right] \tag{9}$$

whence it is apparent that with $N \to \infty$, $T_{m\lambda} \to T_m°$ for any λ. Otherwise said, $T_m°$ is the limiting temperature of melting for a network with infinitely long molecular chains; therefore it is unnecessary to introduce an alternative symbol T_m^* corresponding to $T_{m\lambda,\lambda=0}$ as done in the quoted paper.[3] From the inequality $w(\lambda,T) \geq 0$ we may derive the general upper limit for the crystallization temperature

$$T_{\lim} = T_m°/\left[1 - \frac{4}{\pi}\frac{k_B}{s_f} + \frac{3k_B}{Nfs_f}\right] \tag{10}$$

as well as, neglecting terms of order N^{-1}, the inequality

$$\epsilon(T) \leq 2\left(\frac{8}{3\pi}\right)^{1/2}\lambda/N^{1/2} \tag{11}$$

The last result allows us to expand $w(\lambda,T)$ as a power series of $\lambda/N^{1/2}$, considering $\epsilon(T)$ as being of the same order of magnitude, to obtain

$$w(\lambda,T) = \left[\left(\frac{8}{3\pi}\right)^{1/2}\lambda/N^{1/2} - \epsilon(T)/2\right] + \left[\left(\frac{2}{3\pi}\right)^{1/2}\epsilon(T)\lambda/N^{1/2} - (Nf)^{-1} - \left(\frac{1}{2} - \frac{4}{3\pi}\right)\lambda^2/N\right] \tag{12}$$

within terms of the second degree.

(b) Temperature-Induced Crystallization. After a general thermodynamic investigation of crystallized networks, Wu obtained the following result for the crystalline fraction at $T < T_m°$ (eq 12 of ref 5, $w = 1 - \lambda^*$):

$$w(\lambda,T) = 1 - \left[\frac{\lambda^2(0.5 - \pi^{-1}) + \lambda^{-1}}{-3/2N\epsilon(T)}\right]^{1/2} \tag{13}$$

Unlike at $T > T_m°$, crystallization here implies folded-chain morphology; λ is the macroscopic draw ratio. Through a somewhat different approach an analogous

Table I
Crystallinity Values w Calculated according to Eq 12[a]

		λ		
	ϵ	1.0	2.0	3.0
$N = 100$	0.2	−0.02	0.08	0.18
	0.3	−0.08	0.02	0.13
	0.4	−0.15	−0.04	0.06
$N = 50$	0.3	−0.04	0.11	0.25
	0.4	−0.11	0.04	0.19
	0.5	−0.19	−0.03	0.13

[a] Values of λ, N, and $\epsilon(T)$ are specified. [b] Resulting negative values of w are to be interpreted as $w = 0$. As examples, roughly identifying the statistical segment of *cis*-1,4-polybutadiene with one monomeric unit[3] (s_f = 8.1 cal mol^{-1} K^{-1},[9] $T_m{}^\circ$ = 275 K[10]) and taking $T = T_m{}^\circ + 50 = 325$ K, $\epsilon(T)$ is 0.42 (from eq 8′). In the case of *cis*-polyisoprene, with the same assumptions, s_f = 3.45 cal mol^{-1} K^{-1}, $T_m{}^\circ$ = 301 K,[8] T = 351 K, and ϵ = 0.19.

result was obtained more recently by Smith (eq 16, ref 6).

Discussion and Concluding Remarks

It is well-known that a good rubbery material must be characterized by an ideal melting point in the vicinity of, or slightly lower than, room temperature; this is, in fact, a mandatory requisite for the material to crystallize easily under strain while keeping an amorphous structure otherwise. Accordingly, throughout the present discussion *we will assume $T_m{}^\circ$ as a fixed quantity*, while considering s_f as a variable parameter within the ideal population of all the "good" rubberlike polymers. From 8–13 the following conclusions may be drawn:

(i) At $T > T_m{}^\circ$, a decrease of the melting entropy per segment s_f (hence of $\epsilon(T)$) reduces the lower limit of $\lambda/N^{1/2}$ at which incipient crystallization takes place while increasing the amount of crystallinity for a given $\lambda/N^{1/2}$ (see eq 12 and Table I).

(ii) Again at $T > T_m{}^\circ$, a decrease of s_f increases the temperature of incipient crystallization for a given $\lambda/N^{1/2}$ (see eq 9) and also increases the upper temperature limit at which crystallization may appear (see eq 10).

(iii) At $T < T_m{}^\circ$, the quantity $-\epsilon(T)$, which may be interpreted as the thermodynamic driving force toward thermal crystallization in thermal energy units, decreases with a decrease of s_f (see eq 8′); consequently, the temperature-induced crystallinity $w(\lambda,T)$ of eq 13 also decreases.

(iv) The effect of the change in network connectivity upon crystallization is usually negligible in that it is related to terms of the second order in $N^{-1/2}$ (see terms containing Nf in the above equations).

In light of the above remarks we may now proceed to the following more general considerations:

(1) Strain-induced crystallization is beneficial to rubber performance in that it increases its ultimate properties. It appears quite reasonable therefore that the higher the increase of crystallinity and the melting point with elongation, the better the ultimate behavior of the rubber at ordinary or higher temperatures.

(2) Conversely, temperature-induced crystallization is detrimental to elastomer performance in that it causes an undesirable hardening when the sample is cooled below its isotropic melting point.

(3) The seemingly conflicting requirements of enhancing strain crystallization and of hampering temperature-induced crystallization can be satisfied by molecular structures with *a small melting entropy per statistical segment s_f*. In fact, a small s_f induces the favorable effects listed in points i–iii of the preceding section: it increases the crystallinity for a given temperature and strain, expanding the temperature range in which strain-induced crystallization is observed and reducing temperature-induced crystallization below $T_m{}^\circ$.

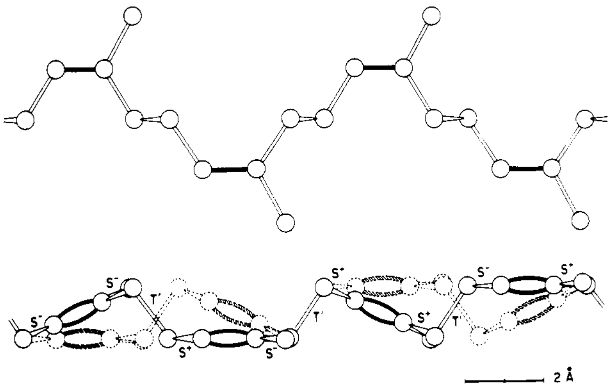

Figure 1. Two side views at right angles of a *cis*-1,4-polyisoprene molecule in the crystalline state, showing conformational disorder as suggested by Corradini et al.[12,14] (Hydrogen atoms omitted.)

(4) It is remarkable that *cis*-1,4-polyisoprene fulfills the requirements expressed in (3) quite well and, e.g., better than the stereochemically analogous *cis*-1,4-polybutadiene. The isotropic melting temperature $T_m{}^\circ$ of polyisoprene is 301 K, with an entropy of melting per monomeric unit equal to 3.45 cal/(mol K).[8] This figure is less than half that of polybutadiene (8.07 cal/(mol K),[9] $T_m{}^\circ$ = 275 K[10]); as for the number of monomeric units within a statistical segment, the approximate figures 1.5 and 2.0 were suggested for polyisoprene[8] and polybutadiene,[9,11] with corresponding melting entropies per segment s_f = 5.2 and 16.1 cal/(mol K), respectively. From eq 10, these figures would give ~300 and ~50 °C as the upper limits for the temperature of crystallization. Proceeding with the comparison, from eq 9 the minimum respective values of $\lambda/N^{1/2}$ required for incipient crystallization at 50 °C above $T_m{}^\circ$ are 0.13 and 0.45, corresponding to λ = 1.5 for polyisoprene and λ = 4.5 for polybutadiene, if the chains comprise 200 monomeric units (i.e., N = 200/1.5 and 200/2, respectively). Even considering for polybutadiene the figure of one monomeric unit per segment, as suggested by one of us to fit some experimental data of strain-induced crystallization,[3] it would still compare quite unfavorably with polyisoprene (the limiting temperature would be ~130 °C and the limiting strain ratio $\lambda \simeq 3.2$).

(5) In principle, a low s_f may be related either to a relatively low entropy in the liquid state or to a relatively high entropy in the solid state, since $s_f = s_l - s_s$. A decrease of the entropy of the liquid state should be related to a decrease of its conformational disorder, for example, by stiffening the chains with bulky side groups, which would be detrimental to rubber elasticity. Consequently, the increase of the entropy in the solid state seems to be the only practical way to achieve the result. This is in fact what happens in polyisoprene, where a substantial amount of conformational disorder in the crystalline state does indeed exist, as shown by Corradini[12] (conformational isomerism; see Figure 1).

In close analogy, the good rubberlike behavior of the butadiene–piperylene copolymers with 1,4-trans enchainment[13] is also related to conformational disorder in the crystalline state. In fact, X-ray investigation of the stretched samples indicates the same crystal structure as that of the conformationally disordered high-temperature polymorph of *trans*-1,4-polybutadiene. It is not surprising that insertion of piperylene units with a random stereochemical structure of the substituted chain atoms may favor the conformational disorder of the chain, according to the model suggested by Corradini and co-workers.[14]

We believe the above considerations represent a potentially useful line of guidance toward the design of improved rubberlike materials.

Acknowledgment. G.A. acknowledges helpful discussions with Dr. M. Košč and with Prof. A. Ziabicki. The present work was supported by the Progetto Finalizzato per la Chimica Fine e Secondaria, CNR, Italy.

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Differential Scanning Calorimetry Analysis of Natural Rubber and Related Polyisoprenes. Measurement of the Glass Transition Temperature

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Received October 20, 1982

ABSTRACT: A DSC examination of natural rubber (NR) and four related *cis*- and *trans*-1,4-polyisoprenes is reported. Onset T_g values for *amorphous* samples of NR and a synthetic cis analogue are 206 and 208 K, respectively, whereas, the three trans isomers studied had lower values in the range 202–203 K. (These values correspond to rapidly quenched samples heated at scan rates of 20 K/min.) The presence of crystallinity has only a marginal effect on the T_g onset value ($T_g \sim +1$ K) but leads to a more diffuse and indistinct glass transition. Annealing of NR at temperatures close to the observed glass transition leads to observation of distinct endothermal peaks associated with molecular relaxation processes. An investigation of the optimal procedure for measurement of T_g values at low temperatures reveals that scan-rate corrections do not enhance the precision of the results. A procedure is recommended where the glass transition is examined at a moderate scan rate of 20 K/min. The same scan rate is also used for instrument temperature calibration to minimize thermal lag errors.

Introduction

The glass transition temperature (T_g) is a fundamental polymer characteristic, the magnitude of which has a determining influence on the bulk properties of the material. Consequently the measurement of T_g has attracted much attention over the years, and those of most important macromolecules have been widely studied by numerous techniques. Natural rubber (NR) and its synthetic analogues have proved no exception, and T_g measurements by the techniques of dilatometry,[1-4] interferometry,[5] refractive index,[6] thermomechanics,[7,8] NMR,[9,31,32] adiabatic calorimetry,[10] and DSC[11-15,26-30] have been reported (Table I). Correlation of the various literature results is complicated by the time-dependent nature of the glass transition phenomenon, by differences in the thermal histories and purity of the samples, and by variations in experimental procedures (e.g., temperature calibration) and interpretation of the raw data. Thus for NR measured T_g values, as determined by methods of similar time scale, range from 195 to 211 K, whereas for high molecular weight synthetic and naturally occurring *trans*-1,4-polyisoprenes (TPI) T_g values in the range 200–213 K have been reported. Although some aspects of microstructure have been studied,[14,15] the effect of cis/trans isomerization on T_g has not been unambiguously established especially as apparent differences reported in the literature may be attributed to variations in the morphology of the samples.

In recent years DSC has emerged as a rapid, relatively precise, and increasingly popular technique for the determination of polymer T_g values. However, there is to date little uniformity as to the measurement or reporting of such values particularly with regard to parameters such as thermal pretreatment, temperature calibration, scan rate, and specification of T_g value (onset or midpoint).

In light of the above, the present work had dual objectives: (i) the determination of unequivocal values for the T_g of naturally occurring and synthetic *cis*- and *trans*-1,4-polyisoprene; (ii) the establishment of optimal procedures for the DSC determination of subambient T_g values.

Experimental Section

Materials. Natural rubber (DPNR grade) and gutta-percha were native Malaysian samples provided by courtesy of the Rubber Research Institute of Malaysia. The synthetic *trans*-1,4-polyisoprene (TPI) and balata were kindly supplied by Dunlop Ltd., U.K.

The synthetic *cis*-1,4-polyisoprene (NATSYN 2200) was kindly donated by Goodyear, U.S.A., who indicated an isomeric purity of 97–98%.

The intrinsic viscosity $[\eta]$ of the various samples at 30 °C in toluene were as follows: DPNR (7.3 dL/g); gutta-percha (1.43 dL/g); TPI (3.0 dL/g); balata (1.7 dL/g); natsyn (3.8 dL/g).

DPNR and the natural and synthetic *trans*-polyisoprene showed no detectable steric impurities by ^{13}C NMR.

Purification of the above samples by reprecipitation from toluene and vacuum-drying showed no discernible affect on measured T_g values.

DSC Measurements. All measurements were made with a Perkin-Elmer DSC-2C equipped with a liquid nitrogen subambient cooling accessory and employing helium as purge gas. In order to ensure good reproducibility the liquid nitrogen reservoir was filled 2 h before calibration and maintained approximately

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