# Synthesis of crosslinked polyisoprenes with a domain structure

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By using linear optimization of chemical processes crosslinked polyisoprenes were prepared from isoprene, strongly intramolecular crosslinked poly(divinylbenzene-co-ethylvinylbenzene) microgels and poly(isoprenyldilithium) as initiator. The extent of microphase separation was determined by swelling and compression measurements. A model for the domain structure of crosslinked polyisoprenes is proposed.

**(Keywords: crosslinked polyisoprene; domain structure; swelling properties; elastic modulus; crosslinking)**

## INTRODUCTION

An application of reactive microgels such as poly(divinylbenzene) or poly(ethylene dimethacrylate) in the formation of polystyrene networks was reported by Funke[1-5], who confirmed that reactive microgels could act as multifunctional crosslinking agents in radical initiated system. Walczyński and Świątły[6] investigated the application of reactive poly(divinylbenzene-co-ethylvinylbenzene) microgels and styrene in a reaction initiated with *n*-butyllithium. Funke *et al.*[2] observed phase separation in their polystyrene networks.

Here we report on the preparation of polyisoprene elastomers that exhibit the properties both of a block copolymer of the ABA type and of a crosslinked polymer. Crosslinked polyisoprene was synthesized in the reaction of isoprene and reactive poly(*m*-,*p*-divinylbenzene-co-*m*-*p*-ethylvinylbenzene) microgels (DEMs) initiated with oligo(isoprenyldilithium). It has been demonstrated by swelling and mechanical measurements that crosslinked polyisoprenes have a domain structure.

## EXPERIMENTAL

### *Materials*

Isoprene (Fluka, Switzerland) was dried over $CaH_2$ and distilled under argon.

The reactive microgels (average content of vinyl groups, $x_{DEM} = 2.55$ mmol g$^{-1}$) of small hydrodynamic volume (inherent viscosity in $CCl_4$ at 25°C, 0.031 cm$^3$ g$^{-1}$, and of small $\bar{M}_n$ (2300 g mol$^{-1}$) consisting of 80 wt% of *m*-,*p*-divinylbenzene and of 20 wt% of *m*-,*p*-ethylvinylbenzene, which was synthesized as described elsewhere[7], were dispersed in isoprene. The average functionality of DEMs, $f$, equals 7 and was calculated from the simple dependence:

$$f = x_{DEM}\bar{M}_n \qquad (1)$$

Oligo(isoprenyldilithium)[8] was prepared in a glass reactor that had been annealed at 403 K, filled with argon (dry and oxygen- and carbon dioxide-free), and washed with a solution of n-butyllithium and then with cyclohexane previously dried over sodium-potassium. 0.69 g of lithium and 100 cm$^3$ of white paraffin oil were heated at 464 K and vigorously stirred to form a lithium dispersion. The dispersion was cooled to 294 K and washed with diethyl ether (previously dried over sodium–potassium) after which the white paraffin oil was removed. At 253 K, 200 cm$^3$ of diethyl ether and 14.2 g of 1-methylnaphthalene were added to the reactor. Its contents were stirred for 24 h. Then 27.2 g of isoprene was added in a few portions. The diethyl ether was removed and 250 cm$^3$ of cyclohexane added. The concentration of lithium in the solution of oligo(isoprenyldilithium) was 0.71 mol dm$^{-3}$.

### *Synthesis of crosslinked polyisoprenes*

6.8 g of isoprene and 2 cm$^3$ of a solution of oligo(isoprenyldilithium) were added to the reactor, which had been pretreated as described above. The reaction was carried out at 293 K under argon for 100 minutes, i.e. to $\sim 65\%$ conversion. The resulting solution of oligo(isoprenyldilithium) ($\bar{M}_n = 5900$ g mol$^{-1}$ and $\bar{f}_n = 1.96$) in isoprene was cooled to 285 K and isoprene and DEM–isoprene dispersion were added. The contents of the reactor were vigorously stirred. After a few tens of seconds the system gelled. The reaction was continued at 323 K. After 96 h the reaction was stopped with 2 cm$^3$ of 0.01 wt% solution of phenyl-2-naphthylamine in methanol.

The samples of crosslinked polyisoprenes were extracted with benzene in a Soxhlet extractor and dried under vacuum to constant weight. The dry samples of polymer were weighed before and after extraction in order to determine the crosslinking efficiency.

The crosslinked polyisoprenes were given identification symbols of the form X DEM-PI, where X is the number

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denoting the percentage of DEM in the crosslinked polyisoprenes (PI).

*Preparation of a reference-standard natural rubber vulcanizate*

The series of rubber mixtures, consisting of natural rubber and dicumyl peroxide, were prepared using a laboratory roll mill. The mixtures were vulcanized at 413 K for 0.5 h. The compression experiments were carried out at 298 K. The vulcanizate for which the elastic modulus had a value close to that of 4.2 DEM-PI sample was selected; its weight composition was: natural rubber, 100 parts; dicumyl peroxide, 1 part.

*Equilibrium swelling measurements*

Equilibrium degree of swelling, $q_e$, is defined as:

$$q_e = (V_p + V_s)/V_p \tag{2}$$

Additivity of the polymer volume, $V_p$, and the volume of solvent, $V_s$, is assumed.

Equilibrium degrees of swelling were calculated according to:

$$q_e = 1 + m_s d_p / m_p d_s^t \tag{3}$$

where $m_s$ is the mass of solvent in the swollen sample, $d_p$ is the sample density, $m_p$ is the mass of dried sample, $d_s^t$ is the density of solvent at the temperature, $t$.

Samples of 0.5–1 g of polymers were swollen in isooctane or benzene at 298–328 K. The samples were left in solvents for 48 h, which was sufficient for the samples to reach equilibrium[9]. Each swelling measurement was repeated five times and the average value of the degree of swelling calculated. The results were reproducible within $\pm 0.05$ of $q_e$.

*Compression measurements*

The compression measurements were carried out using the apparatus with a thermostatically controlled chamber, equipped with a compression piston. Cylindrical samples of polymer were compressed with a force, $P$, of 2–100 N. The strain, $\Lambda$, was recorded by a micrometer sensor with accuracy of $\pm 0.01$ mm. The elastic modulus, $G$, was calculated according to:

$$\sigma = FG(\Lambda - \Lambda^{-2}) \tag{4}$$

where $\sigma = P/s$, $s$ is the surface of the undeformed sample, $G = nRT$, and $n$ is the crosslink density, assuming the front factor, $F$, to be unity. The results were reproducible within $\pm 0.05$ MPa.

## RESULTS AND DISCUSSION

*Optimization of the reaction of isoprene and the divinylbenzene–ethylvinylbenzene microgels*[9]

To determine the optimum quantities of substrates in the reaction of isoprene and DEMs, a procedure for optimization of chemical processes[10] was applied. The crosslinking efficiency, $E_c$, defined as the gel fraction in the crosslinked polyisoprenes, was used as the criterion to be optimized. The following ranges of substrate quantities were studied: isoprene, from 0.176 to 0.294 mole ($x_1$ factor); oligo(isoprenyldilithium), from 1.00 to 1.50 mmol of $Li^+$ ($x_2$ factor); DEMS, from 0.1 to 0.5 g ($x_3$ factor). The regression equation (5) was obtained after a full factorial experiment ($2^3$ scheme) had been made.

$$y = 40.76 + 13.24x_1 - 8.52x_2 + 25.57x_3 - 6.23x_1x_2 + 5.23x_2x_3 + 7.69x_1x_2x_3 \tag{5}$$

From equation (5) it is concluded that the most important factor is the quantity of DEMs. The next most important one is the quantity of isoprene. The quantity of oligo(isoprenyldilithium) and the cross effects are less significant. Further investigations concentrated on the influence of the quantity of DEMs on the crosslinking efficiency.

According to the results of analysis of the regression equation (5) a constant quantity of isoprene (0.294 mol) and oligo(isoprenyldilithium) (1.00 mmol of $Li^+$) were used in the preparation of polyisoprene samples to carry out the swelling and compression measurements. An increase of the content of DEMs from 0.9 to 5.5 wt% in the reaction mixture brings about a corresponding increase in the crosslinking efficiency, as was expected (*Figure 1*).

*Equilibrium swelling of the crosslinked polyisoprenes*

Nierzwicki *et al.*[11] demonstrated that microphase separation of urethane elastomers is reflected in the swelling properties. Since the existence of microphase separation in crosslinked polyisoprenes was also expected, the investigated samples were swollen in benzene or in isooctane.

Typical dependences of equilibrium degree of swelling on temperature ($q_e$–$T$) for crosslinked polyisoprene are shown in *Figure 2*, from which it is seen that at a certain temperature the slope of the $q_e$–$T$ dependence increases suddenly. In the opinion of the authors this increase indicates microphase separation in the investigated samples.

As is known, below a certain critical temperature the phases do not mix, because the enthalpy term dominates over the entropy term in the equation for the free energy of mixing. Beyond the critical temperature, already defined for block copolymers by Leary and Williams[12,13] and called by them the separation temperature, $T_s$, microphase separation disappears. The phenomenon also occurs in the swollen state. It may be interpreted physically that

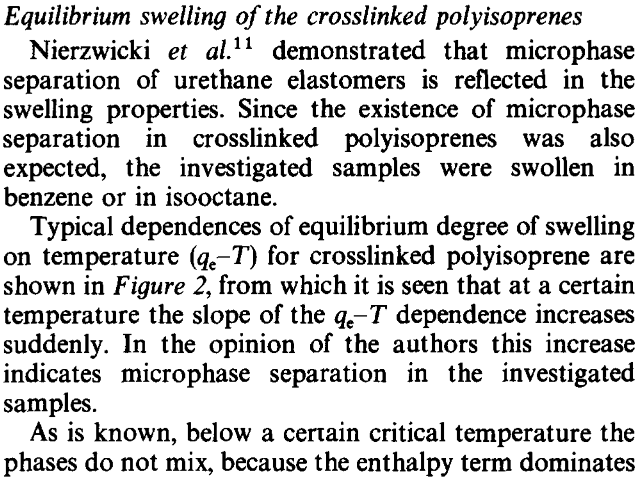

**Figure 1** Crosslinking efficiency vs. microgel content in crosslinked polyisoprenes

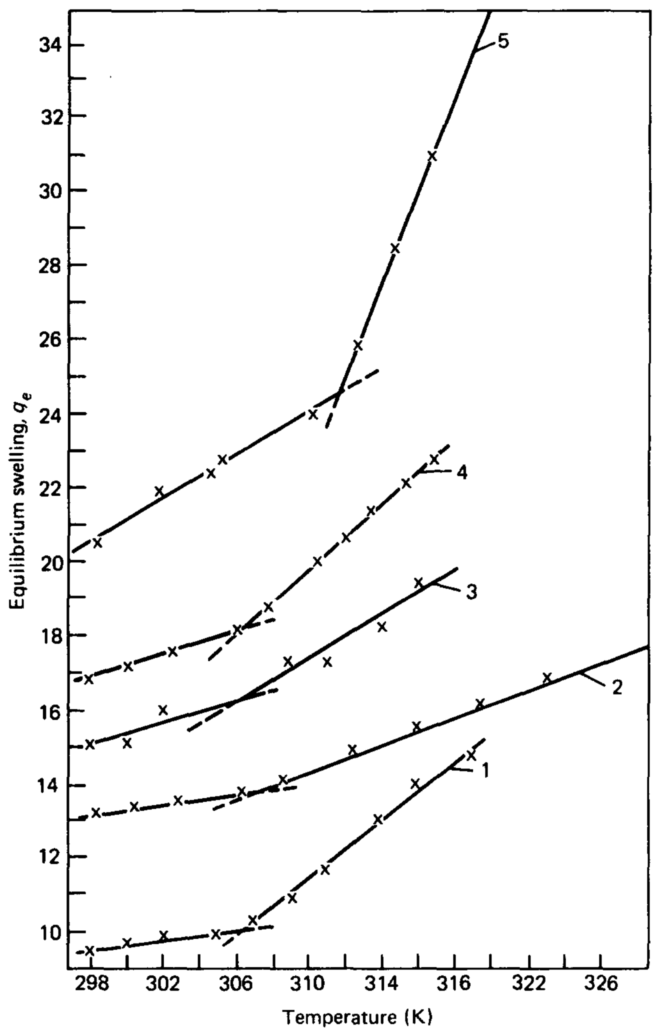

**Figure 2** Equilibrium degree of swelling of crosslinked polyisoprene at different temperatures. (1) 5.5 DEM-PI in benzene; (2) 3.0 DEM-PI in isooctane; (3) 4.2 DEM-PI in benzene; (4) 3.0 DEM-PI in benzene; (5) 2.3 DEM-PI in isooctane

solvent primarily swells the matrix and only, after reaching $T_s$, does it swell the domains.

Below $T_s$, the change of enthalpy of mixing, $\Delta H_m$, for the matrix–solvent system is less than $\Delta H_m$ for the domain–solvent system. Since $\Delta H_m$ is directly proportional to the polymer–solvent interaction parameter, $\chi$, a significant change of $\chi$ at $T_s$ is expected. To demonstrate this change the values of $\chi$ were calculated according to the Flory–Rehner equation[14]:

$$\chi=\frac{(5/6)+(8/9)q_e^{-1}+(11/12)q_e^{-2}+(14/15)q_e^{-3}}{(5/3)+q_e(\delta q_e/\delta T)^{-1}T^{-1}} \qquad (6)$$

These values at different temperatures are shown in *Table 1*. It is easily seen that at $T_s$ the values of $\chi$ jump about 0.02–0.09 for all the investigated polymer–solvent systems. This change indicates that solvent begins to swell domains of different content from the matrix, which consists of pure polyisoprene chains only.

The substrates used in the synthesis of the crosslinked polyisoprenes would indicate that the domains consist only of DEMs. However, the three following features are not in line with this conclusion. First, the increase of the slope of the $q_e$–$T$ dependence by a factor of more than two (*Figure 2*) is observed, in spite of small hydrodynamic volume of DEMs and their strong intramolecular cyclization. Secondly, the increase of the slope occurs for both benzene and isooctane, although isooctane is poor solvent for DEMs. Thirdly, above $T_s$ the values of $\chi$ for isooctane–crosslinked polyisoprene systems are close to 0.50 (*Table 1*), although on comparison with the value of $\chi$ for the isooctane–polystyrene system (*Table 2*)* the system investigated would be expected to exhibit $\chi$ at least greater than 1. The comparison for the benzene systems leads to similar conclusions, but small differences between $\chi$ for natural rubber–benzene and polystyrene–benzene systems* make the simple inference difficult. The contradiction may be removed if it is assumed that the domains are composed not only of DEMs but also of densely packed polyisoprene rings.

By considering the domains as entities consiting of polyisoprene rings and DEMs an attempt can be made to estimate their composition. To find an equation describing the polymer–polymer mixture–solvent interaction parameter, $\chi_{mix}$, it has been assumed that the solubility parameters of the mixture components, $J$, are linked by the expression:

$$J_{mix}=\phi_1 J_1+\phi_2 J_2 \qquad (7)$$

where $J_{mix}$ is the solubility parameter of the polymer–polymer mixture and $\phi$ is the volume fraction of polymer.

The assumption was made by analogy with the expression for $J_{mix}$ of the solvent–solvent mixture[15]. The solubility parameters of polymer, $J$, and solvent, $J_A$, and the polymer–solvent interaction parameter, $\chi$, are linked by the equation[16]:

$$(J-J_A)^2=RT\chi/V_A^0 \qquad (8)$$

where $V_A^0$ is the molar volume of solvent.

**Table 1** Polymer–solvent interaction parameters, $\chi$, and values of the 'effective' crosslink density, $n$, calculated from the Flory–Rehner equation, below and above the separation temperature, $T_s$

| Solvent | Sample density ($g\ cm^{-3}$) | Content of microgels (wt%) | $\chi$ |  | $10^5\ n$ ($mol\ cm^{-3}$) |  |
|---|---|---|---|---|---|---|
|  |  |  | $T<T_s$ | $T>T_s$ | $T<T_s$ | $T>T_s$ |
| Benzene | 0.917 | 2.3 | 0.47 | 0.49 | 0.15 | 0.05 |
|  | 0.911 | 3.0 | 0.43 | 0.49 | 1.26 | 0.40 |
|  | 0.910 | 4.2 | 0.44 | 0.48 | 1.47 | 0.65 |
|  | 0.909 | 5.5 | 0.45 | 0.53 | 3.45 | 0.14 |
| Isooctane | 0.917 | 2.3 | 0.45 | 0.50 | 0.39 | 0.07 |
|  | 0.911 | 3.0 | 0.39 | 0.47 | 2.13 | 0.09 |
|  | 0.910 | 4.2 | 0.39 | 0.48 | 2.63 | 0.10 |
|  | 0.909 | 5.5 | 0.44 | 0.52 | 5.07 | 1.26 |

**Table 2** Polymer–solvent interaction parameters for natural rubber and polystyrene in benzene or isooctane

| System | $\chi$ | Temperature (K) | Reference |
|---|---|---|---|
| Natural rubber–benzene | 0.40–0.46 | 298 | 18 |
| Polystyrene–benzene | 0.43–0.46 | 298–303 | 18 |
| Natural rubber–isooctane | 0.5 | 298 | 18 |
| Polystyrene–isooctane | 1.4 | 298 | 17 |

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* The values of $\chi$ for divinylbenzene–ethylvinylbenzene copolymer have not been found and therefore the values of $\chi$ for polystyrene were considered.

Solving equation (8) gives:

$$J = J_{\rm A} \pm \sqrt{\frac{RT\chi}{V_{\rm A}^0}} \tag{9}$$

After substituting $J_1$ and $J_2$ for the components of the polymer–polymer mixture in equation (7) the following expression is obtained:

$$(J_{\rm mix} - J_{\rm A})^2 = RT/V_{\rm A}^0(\phi_1\sqrt{\chi_1} + \phi_2\sqrt{\chi_2}) \tag{10}$$

Comparison of equations (8) and (10) leads to the final expression:

$$\chi_{\rm mix} = (\phi_1\sqrt{\chi_1} + \phi_2\sqrt{\chi_2}) \tag{11}$$

For calculations the data for isooctane systems have been used. The value of $\chi_2$ is set at 1.4 (ref. 17) and $\chi_{\rm mix}$ and $\chi_1$ are taken from *Table 1*. Thus, it has been estimated that the domains consist of ~10 vol% of DEMs and ~90 vol% of polyisoprene rings.

The change of crosslink density of the samples beyond $T_s$ is interesting. The values of the 'effective' crosslink densities, *n*, of the polyisoprenes studied were calculated from the Flory–Rehner equation[14] assuming that functionality of the domains is so high that the term $2/fq_{\rm c}$ in this equation is negligibly small. The results of the calculations, shown in *Table 1*, are not the absolute values of the crosslink densities, because crosslinked polyisoprenes are heterogeneous and therefore do not fulfil the assumptions of the classical statistical theory of rubber elasticity. However, the values can be compared among themselves. The higher the content of DEMs the higher is the crosslink density of the polyisoprenes investigated, as expected, because the DEMs play the role of crosslinking agent. At $T_s$ the value of the 'effective' crosslink density of polyisoprene samples decreases several times. It can be attributed to a decay of the interactions between domains and matrix.

During preparation the DEMs are probably suspended in isoprene as agglomerates and individual particles, because isoprene does not swell the DEMs. This can be concluded from the difference between the solubility parameters of isoprene (14.8 $\rm MPa^{1/2}$)[19] and divinylbenzene–styrene copolymer (18.6 $\rm MPa^{1/2}$)[20], which is close to 4.2 $\rm MPa^{1/2}$. The solubility parameter of chemically similar divinylbenzene–styrene copolymer was compared, because a value for divinylbenzene–ethylvinylbenzene copolymer has not been found. In the studied reaction system DEMs, composing the agglomerate, can react together forming multifunctional particles.

### *The thermal dependence of elastic modulus for crosslinked polyisoprene*

The elastic modulus is a macroscopic quantity that carries information on polymer structure and crosslink density[21]. The thermal dependence of the elastic modulus for crosslinked polyisoprenes and the reference standard (natural rubber vulcanizate) are shown in *Table 3*. The elastic modulus for crosslinked polyisoprene decreases from ~140 MPa at 203 K to ~1 MPa at 217 K, then remains almost constant from 217 to 358 K. Above 217 K the elastic modulus is dependent on the content of DEMs while at lower temperatures this dependence is not observed. The glass transition temperature, $T_g$, of the studied samples is about 208 K (*Table 3*) and is the same, within experimental error, for both polyisoprenes investigated. It corresponds to the $T_g$ of polyisoprene containing about 60 wt% of Z-1,4 microstructure[22]. The microstructure of the crosslinked polyisoprenes was not determined; only the microstructure of poly(isoprenyldilithium) was estimated: Z-1,4, 60 wt%; E-1,4, 25 wt%; 3,4, 15 wt%. However, taking into consideration results of Hsieh's investigations[23], it is believed that crosslinked polyisoprenes obtained with poly(isoprenyldilithium) as initiator have similar microstructures.

The thermal dependence of elastic moduli for the natural rubber vulcanizate is similar to that for crosslinked polyisoprenes, but it is shifted towards lower temperatures. The $T_g$ of the vulcanizate is close to 203 K (*Table 3*), which is consistent with the values given elsewhere[24,25]. The shift of the elastic modulus vs. temperature curve is probably due to a lower content of Z-1,4 microstructure in the crosslinked polyisoprenes than that in natural rubber vulcanizate. However, the shift may be due to the domain structure of the studied samples.

The elastic modulus at 298 K of the natural rubber vulcanizate is close to that of crosslinked polyisoprenes 4.2 DEM-PI and 5.5 DEM-PI (*Table 3*). Assuming the front factor to be close for both natural rubber vulcanizate and crosslinked polyisoprene, it is clear that the 'effective' crosslink densities, calculated from equation (4), are similar. On the other hand, the 'effective' crosslink densities of the natural rubber vulcanizate and crosslinked polyisoprene, calculated from the Flory–Rehner equation, differ significantly (*Table 4*). The authors believe that the differences can be explained by

**Table 3** Elastic modulus, *G* (MPa), of crosslinked polyisoprenes and natural rubber vulcanizate at different temperatures (*T*)

| Temperature (K) | Polyisoprene | | | |
|---|---|---|---|---|
| | 3.0 DEM-PI | 4.2 DEM-PI | 5.5 DEM-PI | Vulcanizate |
| 203 | 134.24 | 140.12 | 144.95 | 14.72 |
| 208 | 52.45 | 60.58 | 45.03 | 1.50 |
| 217 | 1.69 | 0.88 | 1.45 | 0.89 |
| 228 | — | 0.66 | 0.99 | 0.61 |
| 238 | 0.73 | 0.49 | 0.72 | 0.58 |
| 263.5 | 0.37 | 0.42 | 0.57 | — |
| 278 | 0.34 | 0.34 | 0.49 | — |
| 289.5 | 0.24 | 0.26 | 0.33 | 0.31 |
| 298 | 0.25 | 0.31 | 0.34 | 0.31 |
| 308 | 0.21 | — | 0.31 | 0.31 |
| 318.5 | — | 0.29 | 0.24 | 0.31 |
| 328 | 0.18 | 0.24 | 0.25 | 0.34 |
| 338 | — | 0.23 | 0.25 | 0.36 |
| 348 | — | 0.24 | 0.24 | 0.34 |
| 358 | 0.14 | 0.25 | 0.23 | 0.32 |

**Table 4** Effective crosslink density of crosslinked polyisoprene and natural rubber vulcanizate, *n*, calculated from the Flory–Rehner equation (FR) and from elastic moduli (EM) at 298 K

| Sample | $10^5$ *n* ($\rm mol\ cm^{-3}$) | |
|---|---|---|
| | FR | EM |
| 3.0 DEM-PI | 2.18 | 10.1 |
| 4.2 DEM-PI | 2.68 | 12.5 |
| 5.5 DEM-PI | 5.11 | 13.7 |
| Natural rubber vulcanizate | 50.98 | 12.5 |

the presence of domain structure in crosslinked polyisoprene. As mentioned above in swelling measurements below the separation temperature, only the matrix consisting of loosely packed polyisoprene chains swells and thus the crosslink density appears to be low in relation to the value calculated from equation (4), as all elements of structure are active during deformation. Similar reasoning was applied by Eastwood and Pethrick[26] while considering heterogeneous polyurethanes.

### *Perfection of phase separation*

The calculations of the partial enthalpy of dilution, $\Delta\bar{H}_A$, allow estimation of the perfection of phase separation[11]. The values of $\Delta\bar{H}_A$, calculated from equation (12):

$$\Delta\bar{H}_A = \delta[Rq_c^{-2}(\chi - 0.5)]/\delta(T^{-1}) \qquad (12)$$

are shown in *Table 5*. Because of the assumptions involved in the derivation of equation (12) the values of $\Delta\bar{H}_A$ are only approximate. Nevertheless, the changes in $\Delta\bar{H}_A$ should be sufficient to draw conclusions regarding the changes in perfection of phase separation. The partial enthalpy of dilution reflects the thermodynamic interactions between solvent and the polymer and thus depends on the chemical composition of the polymer. Since, as follows from *Table 5*, there is a correlation between $\Delta\bar{H}_A$ and the amount of DEMs in the investigated samples, one can conclude that the amount of DEMs only slightly affects the perfection of phase separation in crosslinked polyisoprenes. The higher is the amount of DEMs, the greater is the perfection of phase separation.

The above conclusion is reinforced by the dependence of elastic modulus on *T*. The existence of the plateau is characteristic for block copolymers[11,26,27]. Bonart[27] confirmed that the more independent of temperature is the modulus, the more complete is the perfection of phase separation. As is seen from *Table 3*, there is a minor difference in the plateau regions of the investigated polyisoprene systems.

### *Model of structure of crosslinked polyisoprenes*[28]

In *Figure 3* a domain model of the structure of the crosslinked polyisoprenes is shown.

During the reaction between isoprene and small amount of DEMs (0.9–5.5 wt%), initiated by poly(isoprenyldilithium), polymer of such structure is formed. Microgels, dispersed in isoprene, occur as individual particles and their agglomerates. In order to relate the structure to the chemistry of the system one has to take into account several different expected reactions:

extension of poly(isoprenyldilithium) chains as a result of the reaction of initiator and isoprene

**Table 5** Partial molar enthalpy, $\Delta\bar{H}_A$ (J mol$^{-1}$), of dilution of the crosslinked polyisoprenes at 298 K

| | Sample | | |
|---|---|---|---|
| Solvent | 2.3 DEM-PI | 3.0 DEM-PI | 4.2 DEM-PI |
| Isooctane | −0.51 | −3.27 | −3.46 |
| Benzene | −0.19 | −1.10 | −1.15 |

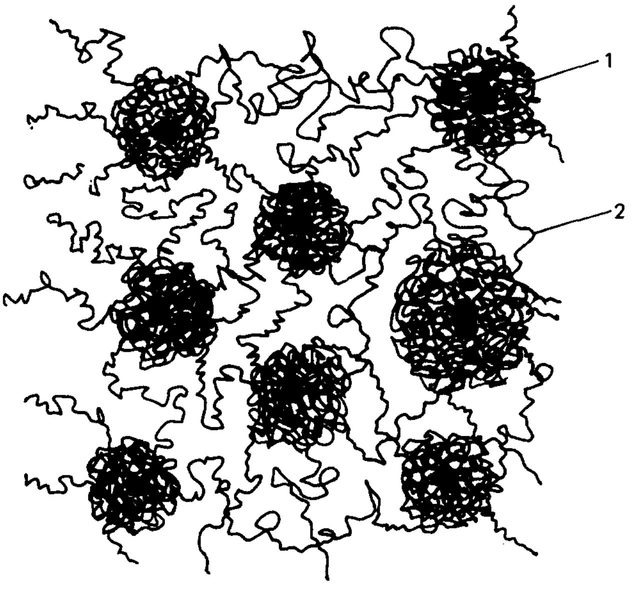

**Figure 3** Model of domain structure of crosslinked polyisoprene: (1) microgels; (2) polyisoprene chains

formation of the multifunctional particles owing to reaction of vinyl groups of different microgels within the agglomerate

formation of polyisoprene chains, leading to the matrix of the network, by the addition of poly(isoprenyldilithium) chains to two different microgels or their agglomerates

formation of polyisoprene rings round the seven-functional microgels or the multifunctional particles owing to the addition of poly(isoprenyldilithium) chains to the same microgel or agglomerate (particle).

The densely packed rings and DEMs subsequently form the domain, where the rings take up ~90 vol% of its volume. Microgels, of small hydrodynamic volume, occupy about 10 vol% of the domain.

The perfection of the phase separation is not large (small values of $\Delta\bar{H}_A$), which is acceptable considering the presence of polyisoprene in both matrix and domains.

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