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Rubber-modified cyanate esters: thermodynamic analysis of phase separation

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Cloud-point curves were determined for blends of a rubber (butadiene–acrylonitrile random copolymer terminated in non-functional groups, NFBN) and a cyanate ester (4,4′-dicyanate-1,1′-diphenylethane, CE). Measurements were made in the initial blend and in partially polycondensed blends (thermal polycyclotrimerization of the CE monomer). Cloud-point conversions and temperatures were determined for different rubber fractions in the initial formulation. A thermodynamic analysis based on a Flory–Huggins equation, taking polydispersity of both components into account, led to the following conclusions. (1) Phase separation was the result of the change in two different contributions to the free energy of mixing: (a) a decrease in the entropic contribution due to the increase in the oligomer size; (b) a decrease in the enthalpic contribution as a result of the decrease in the cohesive energy density of the CE–oligomer in the course of polycondensation. (2) Spinodal demixing was excluded as a possible mechanism of phase separation during polycondensation in solutions containing less than 12% rubber by volume.

(Keywords: cyanate esters; rubber-modified cyanates; phase separation)

INTRODUCTION

Cyanate ester (CE) resins have attracted much interest in recent years owing to their excellent dielectric properties, good dimensional stability and their ability to adhere to metals at high temperatures[1]. The polymer network is generated by the polycyclotrimerization of a dicyanate leading to trifunctional triazine rings (*Figure 1*).

Polymer networks generated from aromatic CE monomers exhibit high glass transition temperatures. These brittle thermosets may be toughened using rubber or thermoplastic modifiers that phase-separate during polycondensation[2].

In this paper, rubber-modified cyanates will be regarded as model systems to perform a thermodynamic analysis of the phase-separation process. The first advantage is that the cyclotrimerization reaction does only involve the CE monomer (i.e. there is no hardener), and it can be carried out without the addition of catalysts or initiators (i.e. by thermal activation). This makes the rubber-modified cyanate ester monomer a truly binary system. The second advantage is that by an appropriate selection of components, the cloud-point curve of the initial formulation may be determined in a temperature range low enough to avoid the polycondensation reaction.

By analysing experimental results in the frame of a Flory–Huggins (FH) equation, taking the rubber polydispersity into account, the interaction parameter of the initial mixture may be obtained. Then, experimental cloud-point conversions may be determined as a function of cure temperature and rubber content. These values may be compared with theoretical estimations arising from the FH equation using the interaction parameter obtained for the initial system and taking the polydispersity generated in the cyclotrimerization reaction into account.

A reasonable fit between experimental results and theoretical estimations should demonstrate that the driving force for phase separation is the decrease in the entropic contribution to the free energy of mixing produced by the size increase of the oligomer distribution. This has been theoretically postulated[3–5] and experimentally proved[6] for rubber-modified epoxies in the frame of a pseudo-binary approach. CE monomers offer a unique opportunity to corroborate this finding in a truly binary system.

However, the cyclotrimerization reaction generates a significant change in the chemical structure owing to the transformation of polar cyanates into less polar triazine rings. The corresponding change in solubility parameters will affect the miscibility with the selected rubber and may produce a shift in cloud-point conversions. This has no analogy with the epoxy chemistry where the polymerization does not bring significant changes in the

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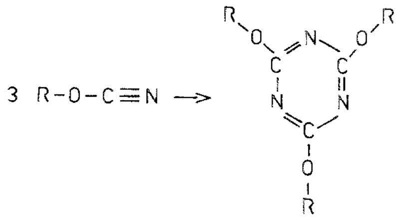


Figure 1 Cyclotrimerization of a cyanate ester leading to a triazine ring

solubility parameters estimated by group contribution methods[7].

In summary, a thermodynamic analysis of experimental cloud-point curves in rubber-modified CE systems will enable us to discuss the origin of the phase-separation process during polycondensation, distinguishing between entropic and enthalpic contributions.

EXPERIMENTAL

Materials

The selected CE monomer is 4,4′-dicyanate-1,1′-diphenylethane (Arocy L10, Ciba-Geigy). Its chemical structure and characteristics are shown in *Table 1*. It is supplied as a low viscosity, undercooled liquid at room temperature, containing 2–3% of monophenol–monocyanate and *ortho–para* substituted isomers.

The selected rubber is a butadiene–acrylonitrile random copolymer terminated in non-functional groups (NFBN; BF Goodrich). Its chemical structure and characteristics are shown in *Table 1*. Average molecular weights and copolymer composition have been reported elsewhere[8]. The number- and mass-average molecular masses are $\bar{M}_n = 2770\,g\,mol^{-1}$ and $\bar{M}_w = 5310\,g\,mol^{-1}$, with a polydispersity index equal to 1.92. The acrylonitrile fraction is 0.176 and the butadiene units are 81.2% 1,4-isomers and 18.8% 1,2-isomers.

Rubber–CE mixtures were prepared at room temperature by manual stirring for 10 min.

Cloud-point determination

Cloud-point temperatures, T_{cp}, of the initial mixtures containing different amounts of rubber were determined using a light-transmission device described elsewhere[7]. The temperature was increased until a homogeneous solution was obtained, kept constant for several minutes and then decreased at a rate of about $1\,K\,min^{-1}$. T_{cp} was determined at the onset time of the light-transmission decrease (*Figure 2A*).

Polycondensations were carried out in the light-transmission device at high temperatures, i.e. typically 180°C. The cloud-point time, t_{cp}, was determined at the onset of the light-transmission decrease (*Figure 2B*). At this time the test tube was taken out of the device and chilled in ice. The cloud-point conversion, p_{cp}, was determined by measuring the residual reaction heat by differential scanning calorimetry (d.s.c.).

Alternatively, the polycondensation was carried out at a constant temperature, and at a particular time before the cloud point the sample was slowly cooled. The cloud-point temperature was determined as indicated in *Figure 2A* and the cloud-point conversion was obtained from d.s.c.

Cloud-point conversion

A Mettler TA 3000 differential scanning calorimeter was used for measuring the residual heats of reaction (ΔH) of partially reacted samples, by scanning from −100 to 360°C (heating rate $10\,K\,min^{-1}$). The cyanate group conversion, p, was calculated by assuming that 100% –OCN groups were reacted when scanning:

$$p = 1 - (\Delta H / \Delta H_0) \qquad (1)$$

where ΔH_0 is the measured heat of reaction for the initial formulation.

RESULTS AND DISCUSSION

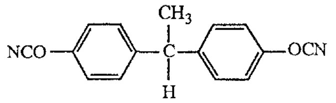
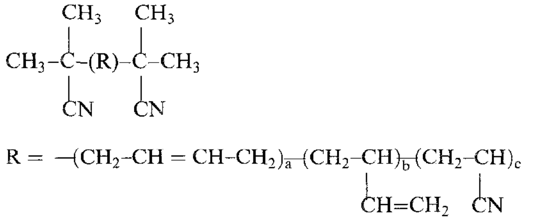
Rubber–CE monomer (initial formulation)

Figure 3 shows experimental values of the cloud-point curve (*CPC*) of the initial formulation. An upper-critical-solution-temperature (*UCST*) behaviour is observed. The maximum of the *CPC* (precipitation threshold) at a volume fraction of rubber close to 0.10 reveals the presence of rubber polydispersity[7].

In order to state the FH equation for this system it is necessary to define the volume of the unit cell. As the molar masses of butadiene (BD) and acrylonitrile (AN) are approximately the same (54 g and 53 g respectively), one of them may be taken as the reference. By selecting BD and using the rubber density (*Table 1*), the reference volume, V_r, was defined as:

$$V_r = (54/0.948)\,cm^3\,mol^{-1} = 56.962\,cm^3\,mol^{-1} \qquad (2)$$

Table 1 Chemical structures and characteristics of the cyanate ester monomer and the rubber

Component	Chemical structure	$\bar{M}_n$ ($g\,mol^{-1}$)	Density ($g\,cm^{-3}$)
Dicyanate		264	1.18
Rubber	 $CH_3-C(CH_3)(CN)-(R)-C(CH_3)(CN)-CH_3$ $R = -(CH_2-CH=CH-CH_2)_a-(CH_2-CH(CH=CH_2))_b-(CH_2-CH(CN))_c$	2770	0.948

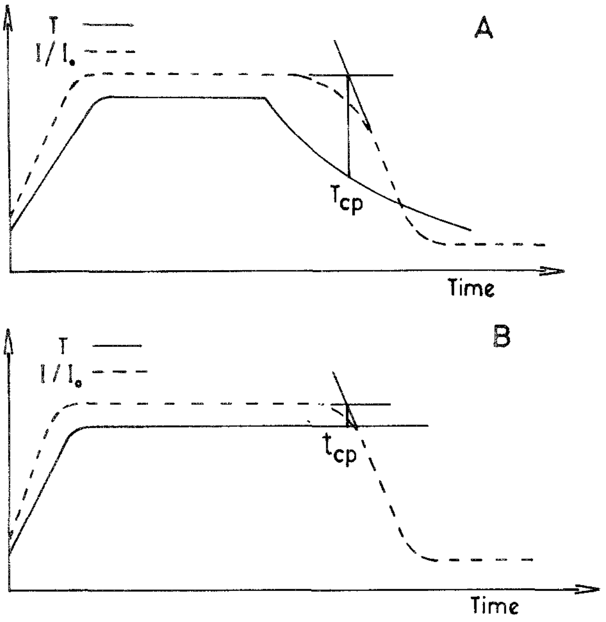


Figure 2 (A) Determination of the cloud-point temperature; (B) determination of the cloud-point time

The rubber molecular-mass distribution may be described by the Schulz–Zimm (SZ) equation[9]:

$$w(x) = [g^{h+1}/\Gamma(h+1)]x^h \exp(-gx) \tag{3}$$

where $w(x)$ is the mass fraction of the $x$mer, $h = [(\bar{x}_w/\bar{x}_n) - 1]^{-1}$, $g = h/\bar{x}_n$, $\bar{x}_n$ and $\bar{x}_w$ are the number and mass average degrees of polymerization, respectively, and Γ is the gamma function. For the selected NFBN rubber, $h = 1.087$, $g = 2.12 \times 10^{-2}$ and

$$w(x) = 3.09 \times 10^{-4} x^{1.087} \exp(-0.0212x) \tag{4}$$

The FH equation written in terms of the Gibbs free energy of mixing per mole of unit cells, ΔG, is given by:

$$\Delta G/RT = \Sigma(\phi_x/x)\ln\phi_x + (\phi_2/V)\ln\phi_2 + \chi\phi_1\phi_2 \tag{5}$$

where R is the gas constant, T is the absolute temperature, ϕ_x is the volume fraction of the $x$mer in the mixture (calculated from equation (4)), $\phi_1 = \Sigma\phi_x$ is the volume fraction of rubber, $\phi_2 = 1 - \phi_1$ is the volume fraction of CE monomer, V is the ratio of CE molar volume with respect to V_r ($V = 3.928$), and χ is the interaction parameter which may be empirically expressed as a function of temperature, polymer volume fraction and the number-average degree of polymerization[10]. The effect of the latter is typically small[11].

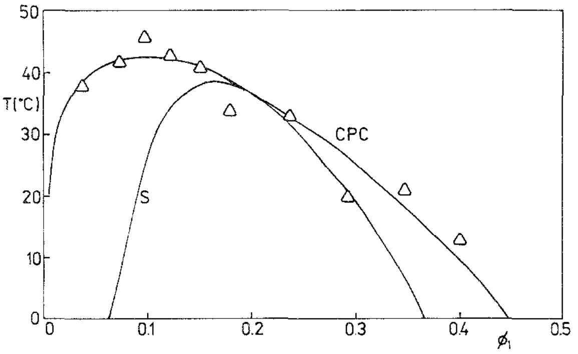


Figure 3 Cloud-point temperature as a function of the rubber volume fraction in the initial formulation (CE–NFBN). Full lines represent the cloud-point curve (CPC) and spinodal curve (S) fitted using the Flory–Huggins equation

Methods for calculating the *CPC* from equation (5) have been proposed and discussed in the literature[10-21]. The procedure developed by Kamide *et al.*[10] was used, incorporating two assumptions: (a) χ is only a function of temperature; (b) the rubber molecular-mass distribution is truncated at $x = 700$ (truncation at higher values did not alter the results). For a particular rubber volume fraction in the initial formulation, calculations led to the χ value at the cloud point, and composition and average molecular-mass distributions in the dispersed phase.

Curve A of *Figure 4* shows a plot of χ *versus* $1/T$ (theoretical χ *versus* experimental $1/T_{cp}$ for the same rubber composition). Points correspond to the compositions shown in *Figure 3*. The following correlation was obtained:

$$\chi = a + b/T(\mathrm{K}) = -0.0372 + 68.692/T(\mathrm{K}) \tag{6}$$

The *CPC* predicted from equation (6) is plotted in *Figure 3*. The fit with experimental values is reasonably good, making it unnecessary to introduce a $\chi(\phi_1)$ dependence. The spinodal curve, given by the following equation:

$$(\bar{x}_w\phi_1)^{-1} + (V\phi_2)^{-1} = 2\chi \tag{7}$$

is also plotted in *Figure 3*.

The composition of the critical point is obtained from:

$$\phi_{1c} = [1 + \bar{x}_w/(V\bar{x}_z)^{0.5}]^{-1} \tag{8}$$

From the SZ distribution, $\bar{x}_z/\bar{x}_w = (h+2)/(h+1)$. Replacing in equation (8), we get $\phi_{1c} = 0.195$.

The resulting interaction parameter may be compared with the value obtained for a solution of the same rubber in diglycidylether of bisphenol A (DGEBA). Experimental cloud points[8] are plotted in *Figure 5*. Curve B of *Figure 4* shows calculated values of the interaction parameter as a function of $1/T$, leading to the following

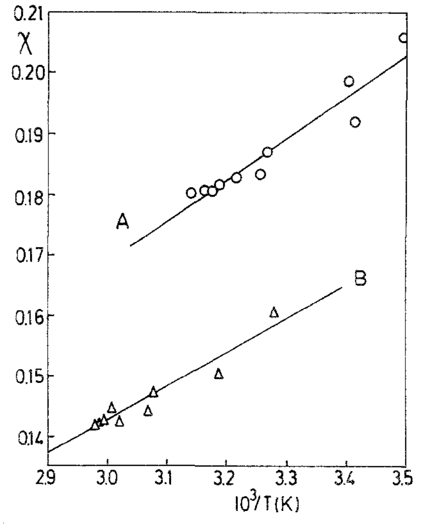


Figure 4 Interaction parameter (calculated) *versus* $1/T_{cp}$ (experimental). Curve A, CE–NFBN before polycondensation; curve B, DGEBA–NFBN formulation

correlation:

$$\chi = -0.0254 + 56.089/T \text{ (K)} \tag{9}$$

The *CPC* and spinodal predicted from equation (9) are plotted as full lines in *Figure 5*. Again, the good fit shows that it is unnecessary to introduce a $\chi(\phi_1)$ dependence for this particular system.

It is interesting to compare the solubility of the rubber (NFBN) in both the cyanate ester (CE) and the epoxy (DGEBA). A direct comparison of experimental cloud-point curves (*Figures 3* and *5*), shows that CE is a better solvent for NFBN than DGEBA, i.e. homogeneous solutions are obtained at lower temperatures. However, *Figure 4* shows that the interaction parameter for the pair CE–NFBN is higher than that for DGEBA–NFBN, i.e. DGEBA should be a better solvent than CE. This apparent contradiction reveals the importance of solvent size in the entropic contribution to the free energy of mixing. Thus, as CE has a lower molar volume than DGEBA, its higher entropic contribution counterbalances the weight of the interaction term and makes CE a better solvent than DGEBA for NFBN.

Phase separation during polycondensation

At reaction temperatures, i.e. higher than 100°C, the initial system is a homogeneous solution that phase-separates in the course of polycondensation. In order to perform a thermodynamic analysis, the polydispersity of the CE polymer must be taken into account.

Assuming an ideal cyclotrimerization[22–25], the oligomer distribution in the pre-gel stage may be described by the following equation[26,27]:

$$w(y) = \{(2y+2)!/[(y+2)!(y+1)!]\}p^y(1-p)^{y+2} \tag{10}$$

where y is the number of triazine rings per molecule (the species with $y = 0$ is the unreacted monomer), $w(y)$ is the mass fraction of the $y$mer, and p is the conversion of cyanate groups.

The Gibbs free energy of mixing per mole of unit cells is expressed as:

$$\Delta G/RT = \Sigma(\phi_x/x)\ln\phi_x + (1/V)\Sigma[\phi_y/(2y+1)]\ln\phi_y + \chi\phi_1\phi_2 \tag{11}$$

where $\phi_1 = \Sigma\phi_x$ is the volume fraction of rubber, $\phi_2 = \Sigma\phi_y$ is the volume fraction of CE oligomers and $(2y+1)V$ is the ratio of the molar volume of the $y$mer with respect to V_r. Shrinkage produced during polycondensation[28] is neglected in the present analysis.

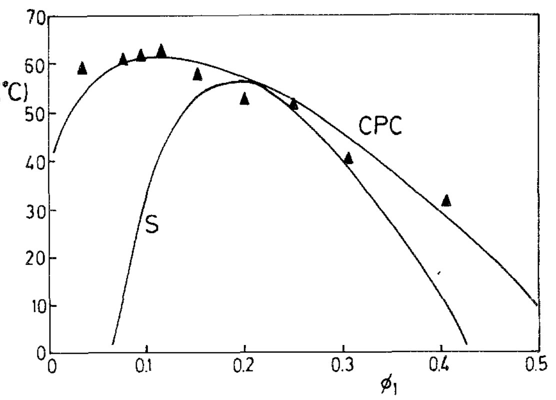


Figure 5 Cloud-point temperature as a function of the rubber volume fraction for a DGEBA–NFBN formulation. Full lines represent the cloud-point curve (CPC) and spinodal curve (S) fitted using the Flory–Huggins equation

For a given conversion p, the ϕ_y distribution was truncated at $y = 107$ (truncation at higher values did not alter the results). The *CPC* was obtained from equation (11) using algorithms developed in the literature[29], adapted for the particular case where χ is not dependent on composition. Solutions gave the value of χ at the cloud point for particular values of conversion and initial rubber concentration.

Experimental values of temperature (T_{cp}) and conversion (p_{cp}) at the cloud point were obtained for various mass fractions of rubber in the initial formulation (*Table 2*). For a given mass fraction of rubber, the increase in the cloud-point temperature with conversion is the result of the increase in the average size of the oligomer distribution and the consequent decrease in miscibility. The calculated values of the interaction parameter at the cloud point exhibit a decreasing trend with T_{cp} (*Table 2*), which is characteristic of *UCST* behaviour.

In order to analyse the possible effect of a change in the enthalpic contribution to miscibility, it is assumed that:

$$\chi = \chi_S + \chi_H = a + b/T \tag{12}$$

where the entropic contribution, $\chi_S = a$, and the enthalpic part of the interaction parameter is $\chi_H = b/T$. Then, if the change in chemical structure, i.e. conversion of cyanate groups into triazine rings, has a bearing on miscibility, χ_H must be a function of conversion. The value of a was kept constant and equal to the value for the initial mixture, i.e. $a = -0.0372$. Values of $b = (\chi - a)T_{cp}$, shown in *Table 2* and represented in *Figure 6*, exhibit a decreasing trend with conversion. This trend is not dependent on the initial fraction of rubber within experimental error.

Therefore, polycondensation affects the miscibility of rubber-modified CE in two different ways: (a) there is a decrease in the entropic contribution to the free energy of mixing (combinatorial terms), a factor that decreases miscibility; (b) there is a decrease in the value of the interaction parameter arising from the change in chemical structure, a factor that increases miscibility. Phase separation takes place owing to the predominance of the first factor over the second one. But the presence of the second factor shifts the cloud-point conversion to higher values than those calculated by assuming that χ keeps the value of the initial formulation, i.e. assuming that b remains constant.

Figure 7 shows calculated cloud-point curves for $\chi = \chi_0$ (value for the initial formulation) and $\chi = \chi(p)$. This function was obtained by fitting $b(p)$ through a third order polynomial regression, as shown in *Figure 8*. This led to:

$$b(K) = 68.272 - 121.83p + 262.80p^2 - 271.38p^3 \tag{13}$$

Equation (13) should not be extrapolated beyond $p = 0.35$.

Also plotted in *Figure 7* is a set of experimental values of cloud-point conversions measured at 180°C in the light-transmission device, followed by d.s.c. scans. Experimental values are reasonably predicted using the functionality of the interaction parameter with

Table 2 Experimental values of the initial rubber mass fraction (w_1), conversion (p_{cp}) and temperature at the cloud point (T_{cp}), and values of the calculated interaction parameter (χ) and the coefficient related to its enthalpic contribution, $b = (\chi - a)T_{cp}$

w_1	p_{cp}	T_{cp} (K)	χ	b (K)	w_1	p_{cp}	T_{cp} (K)	χ	b (K)
0.03	0	307	0.183	67.6	0.15	0	307	0.183	67.7
	0.062	317	0.156	61.2		0.013	311	0.175	66.1
	0.175	356	0.114	53.9		0.018	322	0.173	67.7
	0.240	388	0.095	51.2		0.036	319	0.162	63.7
	0.304	420	0.078	48.2		0.077	342	0.142	61.2
	0.335	457	0.070	49.0		0.080	325	0.140	57.7
						0.084	353	0.139	62.2
0.06	0	315	0.181	68.7		0.206	373	0.092	48.3
	0.096	331	0.138	57.9		0.212	413	0.090	52.7
	0.163	364	0.113	54.8		0.235	427	0.084	51.5
	0.235	404	0.091	51.8		0.294	457	0.067	47.7
	0.333	458	0.065	47.0		0.325	457	0.060	44.2
0.10	0	316	0.181	68.9	0.20	0	306	0.187	68.7
	0.062	327	0.150	61.1		0.063	321	0.149	59.9
	0.111	358	0.129	59.4		0.099	352	0.132	59.4
	0.209	396	0.095	52.1		0.210	393	0.089	49.6
	0.277	451	0.075	50.7		0.280	457	0.068	48.2
	0.316	457	0.065	46.9					

conversion, i.e. equations (12) and (13), in the FH equation. However, if a constant χ is assumed, predicted cloud-point conversions are about half of the experimental values. This means that changes in both entropic and enthalpic terms contribute significantly to the miscibility of rubber-modified cyanate esters in the course of polycondensation. The situation is different from that for rubber-modified epoxies, where cloud-point conversions could be predicted using the value of χ fitted for the initial formulation[6]. This is due to the relatively small change in the chemical structure during an amine–epoxy polycondensation when compared to the polycyclotrimerization reaction of a small CE monomer.

An additional comment may be made regarding the interpretation of experimental determinations. It is clear that experimental measurements corresponding to the initial formulation are located in the *CPC*, as revealed by the presence of a precipitation threshold at the left of the critical point, arising from the rubber polydispersity (*Figure 3*). This means that a cooling rate in the order of $1\,\mathrm{K\,min^{-1}}$ is low enough to avoid spinodal demixing, at least for compositions that are not close to the critical point. The same situation was assumed to occur when partially reacted mixtures were slowly cooled to provoke phase demixing (results shown in *Table 2*). These results were interpreted using *CPC* calculations, as for the initial formulation. But the third set of experimental results was determined in the course of a polycondensation at 180°C, i.e. a typical reaction-induced phase separation or chemical quenching (*Figure 7*). It is observed that for solutions containing less than 0.12 volume fraction of rubber, phase separation proceeds along the calculated *CPC*. Therefore, the presence of spinodal demixing has to be excluded in this composition range, at least in the initial stages of phase separation. It may be possible, however, to have spinodal decomposition at higher rubber volume fractions, as revealed from *Figure 7*. A study by small-angle X-ray scattering (SAXS)[30] showed a relatively fast phase-separation process for formulations containing 15 wt% NFBN.

The Scatchard–Hildebrand model

A semiquantitative estimation of the $b(p)$ functionality may be obtained through the Scatchard–Hildebrand theory[31], in terms of the solubility parameters (δ) estimated from group contribution methods[32].

For the rubber–CE monomer, $b(0)$ may be written as:

$$b(0) = (V_r/R)[\delta_{CE}(0) - \delta_{NFBN}]^2 \qquad (14)$$

Using $b(0) = 68.272\,\mathrm{K}$ (equation (13)), the experimental difference between the solubility parameters of both components is:

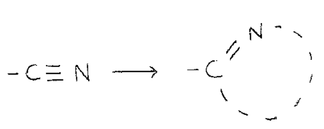
$$[\delta_{CE}(0) - \delta_{NFBN}]_{exp} = 3.1\,\mathrm{MPa}^{1/2} \qquad (15)$$

Values arising from the group contribution method of Small (within ref. 32) are: $\delta_{CE}(0) = 23.0\,\mathrm{MPa}^{1/2}$ and $\delta_{NFBN} = 18.3\,\mathrm{MPa}^{1/2}$. Therefore:

$$[\delta_{CE}(0) - \delta_{NFBN}]_{Small} = 4.7\,\mathrm{MPa}^{1/2} \qquad (16)$$

The transformation of CE into triazine rings leads to a narrowing of the gap between both solubility parameters through the decrease of $\delta_{CE}(p)$ with conversion.

The function $\delta_{CE}(p)$ may be obtained by representing the cyclotrimerization reaction as:



i.e. one-third of a triazine ring.

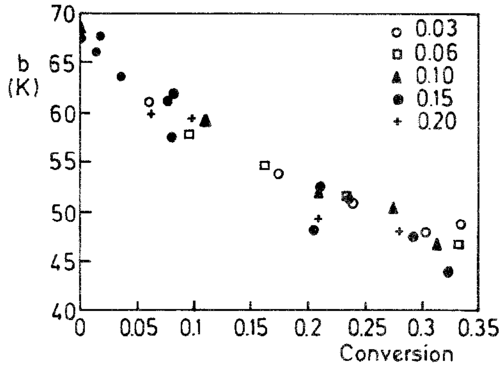


Figure 6 Variation of the enthalpic contribution to the interaction parameter, b (K), with conversion, for different mass fractions of rubber in the initial formulation

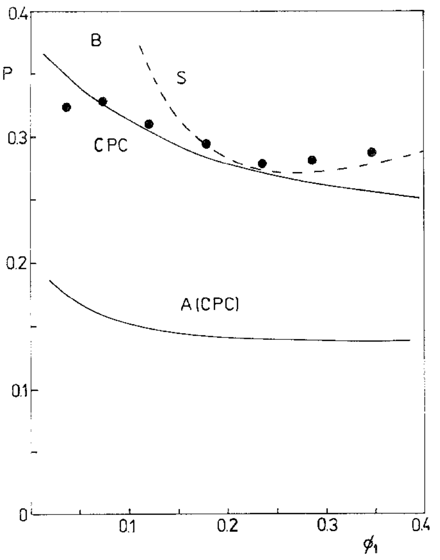


Figure 7 (A) Calculated cloud-point curve at 180°C for $\chi = \chi_0$. (B) Calculated cloud-point and spinodal curves at 180°C for $\chi = \chi(p)$. Points represent experimental values of cloud-point conversions at 180°C

For the ideal polycyclotrimerization[33], the fraction of unreacted monomer at any conversion p is given by $(1-p)^2$, the fraction of monoreacted monomeric units is given by $2p(1-p)$ and the fraction of bireacted units is equal to p^2. Therefore, by calling $E_{\mathrm{coh}}(0)$ the cohesive energy density of the monomer and Δ the decrease in cohesive energy density associated with the reaction of one cyanate group, the cohesive energy density at any conversion p may be calculated by:

$$E_{\mathrm{coh}} = E_{\mathrm{coh}}(0)(1-p)^2 + [E_{\mathrm{coh}}(0) - \Delta]\,2p(1-p) + [E_{\mathrm{coh}}(0) - 2\Delta]p^2 = E_{\mathrm{coh}}(0) - 2p\Delta \qquad (17)$$

and

$$\delta_{\mathrm{CE}}(p) = [E_{\mathrm{coh}}(0) - 2p\Delta]^{1/2} = [\delta^2_{\mathrm{CE}}(0) - 2p\Delta]^{1/2} \qquad (18)$$

Therefore, $b(p)$ may be obtained from:

$$b(p) = (V_{\mathrm{r}}/R)[(\delta^2_{\mathrm{CE}}(0) - 2p\Delta)^{1/2} - \delta_{\mathrm{NFBN}}]^2 \qquad (19)$$

Experimental values shown in *Figure 6* were correlated with an equation of the type

$$b(p) = [(m_1 - m_2 p)^{1/2} - m_3]^2 \qquad (20)$$

The best fit, shown in *Figure 9*, leads to the following values: $m_1 = 2769.31\,\mathrm{K}$, $m_2 = 449.17\,\mathrm{K}$ and $m_3 = 44.46\,\mathrm{K}^{1/2}$. From equations (19) and (20), we obtain: $\delta_{\mathrm{CE}}(0) = 20.1\,\mathrm{MPa}^{1/2}$, $\delta_{\mathrm{NFBN}} = 17.0\,\mathrm{MPa}^{1/2}$ and $\Delta = 32.8\,\mathrm{MPa}$. The extrapolated solubility parameter at complete conversion is $\delta_{\mathrm{CE}}(1) = 18.4\,\mathrm{MPa}^{1/2}$. This reduces the gap between solubility parameters from $3.1\,\mathrm{MPa}^{1/2}$ to $1.4\,\mathrm{MPa}^{1/2}$ at full conversion.

If NFBN is replaced by a modifier (M) exhibiting a δ_{M} higher than $\delta_{\mathrm{CE}}(0)$, such as poly(ether imide) (PEI), the cyanate ester polycondensation will increase the gap between solubility parameters, contributing to the reduction of the modifier miscibility in the reacting system.

CONCLUSIONS

A thermodynamic analysis based on a Flory–Huggins equation was applied to experimental cloud-point determinations in a rubber (butadiene–acrylonitrile random copolymer terminated in non-functional groups, NFBN)–cyanate ester (4,4′-dicyanate-1,1′-diphenylethane) system. The following conclusions were obtained.

1. Phase separation took place in the course of the monomer polycyclotrimerization as a result of the change in two different contributions to the free energy of mixing: (a) a decrease in the entropic contribution (combinatorial terms of the FH equation) due to the increase in the oligomer size (factor promoting phase demixing); (b) a decrease in the enthalpic contribution (part of the interaction parameter) as a result of the decrease in the cohesive energy density of the oligomer and a corresponding decrease in the difference between solubility parameters of both components (factor promoting miscibility).
2. For solutions with a rubber volume fraction less than 0.12, spinodal demixing had to be excluded as a possible mechanism for initiating phase separation along the polycondensation. This mechanism may be present, however, for higher values of the rubber content.

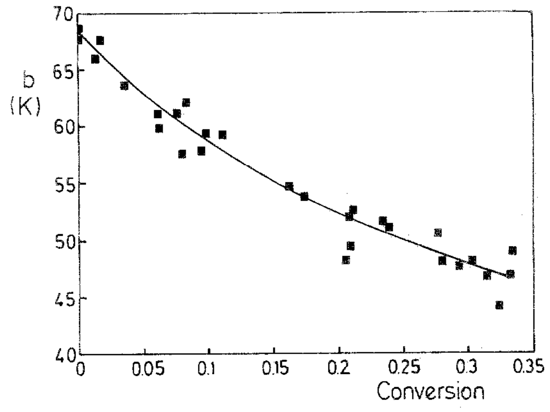


Figure 8 Fitting of a third order polynomial regression to b (K) *versus* conversion

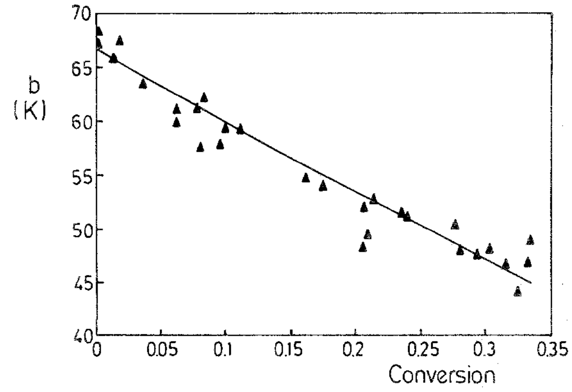


Figure 9 Fitting of an equation representing the Scatchard–Hildebrand model to the values of b (K) *versus* conversion

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