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Proposed solution for the Flory–Charlesby equation for crosslinked polymers and application for 1,2-polybutadiene crosslinked with AIBN and aryl diazide

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ABSTRACT

The derivation and properties of a tractable function that approximates well the solution of the Flory–Charlesby equation for crosslinked polymers with logarithmic normal primary molecular size distribution is presented. This function gives the possibility to determine the crosslinking density, ρ, from measurements of insoluble fraction, what is the only quantitative method that can be applied for postsynthesis crosslinked polymers. Applications to 1,2-polybutadiene crosslinked with AIBN and 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone by heating allowed to obtain information about the gel point as well as about the crosslinking yield and mechanism. In addition, it was found that the temperature where the damping factor in DMA curves is maximum increases with ρ following a second order dependence.

1. Introduction

The estimation of the degree of crosslinking is a rather old problem of continued interest due to several high tech applications like, for example, the crosslinking of reactive resins, clays and lacquers performed by means of electromagnetic and corpuscular particles, to obtain photos and relief images at micro and nanoscale. In addition, the characterization of the crosslinking state of polymers might generate various interesting scientific studies.

Methods for the estimation of the degree of crosslinking can be grouped in two categories: (i) methods applied to polymeric networks obtained by copolymerization of mono- and multifunctional monomers, where the relationships are based on reactivity, functionality and relative concentrations of comonomers, as well as on reaction extent, and (ii) methods based on quantitative and qualitative correlations between measurable parameters and parameters of crosslinked state. Methods of the second group are the sol–gel method, which is based on a theory initially formulated by Flory [1–3] and afterwards completed by Charlesby [4], the swelling ratio method based on the Flory–Rehner equation [5,6], the thermal extension method [7,8], as well as methods based on the influence of the crosslinking on some physical processes, such as the relaxation processes of nuclear magnetic [8,9], dielectric and mechanical [9,10] types. The swelling ratio method is mostly reported in the scientific literature, the effect of crosslinks on mechanical stress–strain curves is especially useful for the characterization of rubbers, and the thermal extension can be applied to thermosetting resins.

Although advantageous due to its simplicity and rather good precision, the sol–gel method is disadvantaged by the fact that the relationship between the measurable parameter, namely the insoluble fraction, g, and the density of crosslinking, ρ, defined as the fraction of crosslinked mers, is mathematically tractable only in some hypothetical cases.

It is worth mentioning the basis of the sol–gel method. Flory [1] showed in 1942 that the gel formation for a polymer with all initial molecules of the same size (the same number of mers), y_0, begins at $\rho_{\min} = 1/y_0$, and the relationship between ρ, g and y_0 is

$$g = 1 - \exp(-\rho g y_0) \tag{1}$$

Stockmayer [11] demonstrated in 1944 that the gel formation for polymers with arbitrary molecular size distribution (MSD) begins at $\rho_{\min} = 1/y_w$ where y_w is the initial weight average degree of polymerization. Then, Flory [2] established in 1947 the following general equation connecting the density of crosslinking, ρ, gel fraction, g, and the initial MSD:

$$g = 1 - \frac{\sum N_i y_i (1 - \rho g)^{y_i}}{\sum N_i y_i} \tag{2}$$

where N_i represents the number of molecules containing y_i monomer units each. Finally, Charlesby [4] has found the following

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general expression for the relationship between gel fraction and crosslinking density for an arbitrary initial MSD:

$$g = 1 - \frac{\sum N_i y_i \exp(-\rho g y_i)}{\sum N_i y_i} \qquad (2')$$

Eqs. (2) and (2′) have been obtained by using the following plausible hypothesis: (i) crosslinking takes place at random, so that ρ is independent of MSD and (ii) the number of crosslinks is small compared with the number of monomers units available for crosslinking.

By numerical solving for the cases of logarithmic normal and Tung-Weibull MSDs, we have found that the Eqs. (2) and (2′) are practically identical, the relative differences between g values calculated with the two equations for different values of ρ and polydispersity parameters being lower than $1/10^6$. Details of the calculation are given in the Appendix. Further on, the name of Flory–Charlesby (F–C) equation will be used for either Eq. (2) or (2′).

The F–C equation cannot be solved analytically. Therefore, currently used expressions for the relationship between ρ and g do not contain molecular polydispersity parameters. While it is true that the density of crosslinking (defined as the fraction of crosslinked mers) is not dependent on the molecular polydispersity, the initial molecular polydispersity parameters must be present into the relation between the crosslinking density and its measurable parameter (fraction of insoluble gel or gel fraction, swelling ratio, thermal extension, Young modulus, etc.). In almost all cases, expressions applicable to initially molecular monodisperse polymers, such as Eq. (1), are used. For these polymers, we recently gave a description of the photocrosslinking state where relationships between crosslinking density, irradiation dose, gel fraction and swelling ratio are presented [12].

Many studies have been dedicated to polymers that undergo simultaneous crosslinking and chain scission when exposed to high energy radiation [13]. The results of these studies are of interest for the production of both radiation stable polymers and easily photodegradable plastics, as well as for materials known as photo, γ-ray, X-ray and electron beam resists. To this aim, Charlesby and Pinner [14] have solved Eq. (2′) for a hypothetical pseudo-random MWD and have applied their theory to radiated polyethylene. Later, Galiatsatos and Eichinger [15] have obtained reliable results for network formation by computer simulation with an original algorithm [16] applicable for polyethylene and other polymer of narrow MSD. Before, Saito et al. [17,18] and Inokuti [19] have developed the Charlesby–Pinner's expression for a realistic MSD, namely the logarithmic normal (log norm) distribution of Wesslau (W) type [20,21]. Their expressions are computer processable but are not mathematically tractable.

In this article we present relationships between ρ, g and molecular polydispersity parameters that fulfill well Eqs. (2) and (2′) for log norm MSDs. The equations were applied for 1,2-polybutadiene (PB) thermally crosslinked with AIBN (azobisisobutyronitrile) and ABC diazide (2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone) to obtain information about the gel point, crosslinking yield and correlation between the crosslinking density and the dynamic mechanical loss peak temperature.

The theory developed in this paper refers to weakly crosslinked systems. Taking into account that the crosslink density cannot be measured by usual physical methods, the equations developed are especially useful for the postsynthesis crosslinked polymers the crosslink density of which cannot be estimated from basic chemistry and the crosslinking mechanism.

2. An approximate solution of Flory–Charlesby equation for polymers with initial log norm MSD: derivation and some characteristics

2.1. Variables and presumable characteristics of the “exact” function

It results from Eq. (2) that the gel fraction, g, depends on the density of crosslinking, ρ, and on the parameters defining the molecular distribution function of the primary polymer, namely y_n and y_w or y_w and y_z or y_w and D ($D = y_w/y_n$). All parameters are defined in the Appendix. Therefore, the gel fraction can be expressed as a function of these variables, for example $g(\rho, y_n, y_w)$ or $g(\rho, y_w, y_z)$ or $g(\rho, y_w, D)$. In general, the gel fraction also depends on other factors. Two of them are the density of entanglements and the so-named thermoreversible gelation [20]. However, the present article only refers to the parameters considered in the Flory–Charlesby's equation.

Presumable characteristics of the function $g(\rho, y_n, y_w)$ would be those given by the dependence $g(\rho)$. Reported in the literature and also demonstrated in this paper is that this dependence is monotonously increasing from zero to the limit value 1. Therefore, the function $g(\rho)$ has a horizontal asymptote at $g = 1$.

Other characteristics of interest for the dependence $g(\rho)$ are those in and near the gel point, where $g = 0^+$. The algebraic expressions of density of crosslinking, gel fraction and slope of $g(\rho)$ (expressions (3)) can be easily found in and near the gel point. The calculus is given in the Appendix.

$$\rho|_{g=0} = \rho_{\min} = 1/y_w \qquad (3a)$$

$$g|_{\rho\to 1/y_w} = 2(z-1)y_n/z^2 y_w \qquad (3b)$$

$$\partial g/\partial\rho|_{\rho\to 1/y_w} = 2(2-z)y_n/z^3 \qquad (3c)$$

$$\partial g/\partial\rho|_{\rho=1/y_w} = 2y_n \qquad (3d)$$

where $z = \rho y_w$.

As mentioned before the expression $\rho_{\min} = 1/y_w$ has been derived many years ago by Stockmayer [11].

Eqs. (3a-3d) are is valid for any kind of MSD of the primary polymer, but the expressions of y_n and y_w are MSD dependent. The expressions for usual distribution functions and for y_n and y_w are given in the Appendix. Polydispersity dependences similar with that in Eq. (3d) have been obtained experimentally [21] and theoretically [22] by Reiser and Pitts for gel curves of photocrosslinking polymers with Wesslau (W) log norm distribution.

2.2. Numerical solution of Eq. (2) for log norm MSD

Eq. (2) was numerically solved for the two types of log norm MSDs (expressions given in Appendix) by using the Mathematica Calculus Program (Wolfram Research). The values of g were determined for $y_0 = 1000$ and various values of ρ and b. The corresponding points (ρ, b, g) will be considered further on as the “exact” solution of Eq. (2). They are plotted in Fig. 1. As know, y_0 is a parameter related to the most frequent degree of polymerization (see Appendix A4), and b is

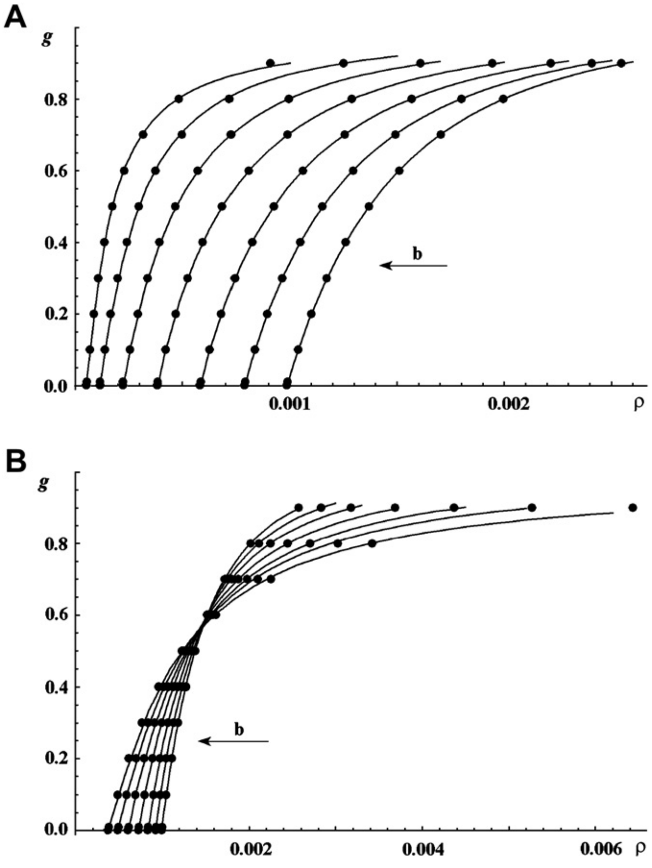

Fig. 1. Dependences of $g(\rho,b)$ for L–K (plots A) and W (plots B) log norm distributions. Coordinates ρ and g have the values obtained by numerically solving the Flory–Charlesby equation for $y_0 = 1000$ and various b values. In the arrow direction, the values of b are 0.1, 0.4, 0.6, 0.8, 1.0, 1.2 and 1,4. The continuous curves represent the proposed function $g(\rho, y_0, b)$ for the same values of y_0 and b.

the dispersity, which is related to the polydispersity index y_w/y_n by Eq. (4).

$$y_w/y_n = \exp b^2 \quad \text{and} \quad b = (\ln y_w/y_n)^{0.5} \tag{4}$$

The polydispersity was varied from $b = 0$, when $y_w/y_n = 1$ (molecularly monodisperse polymers), to $b = 1.4$, when $y_w/y_n = 7.1$.

The numerical solution of F–C equation led to some findings which were very useful for the building of the function proposed as solution of Eq. (2). One observes the following:

(i) g takes the same values when ρ and y_0 are changed but the product ρy_0 is constant. It results that the wanted function should be dependent on the product ρy_0, and not separately on ρ and y_0. For this reason, the numerical solution was carried out only for $y_0 = 1000$.
(ii) The values of $\rho_{\min}$ corresponding to different b values respect the equality $\rho_{\min} = 1/y_w$ with the precision assured by the calculus program used (11 significant digits).
(iii) One observes that the slope in gel point increases with b for the L–K (Lausing–Kraemer) distribution and decreases with b for the W (Wesslau) distribution, therefore, how y_n depends on b at $y_0 = $ constant. For the same value b, the derivative $\partial g/\partial \rho$ has the maximum value in the gel point (where $\rho = \rho_{\min} = 1/y_w$) and tends to zero when $g \to 1$.
(iv) The gel fraction, g, increases monotonously with the density of crosslinking, ρ.

2.3. Building of a function g(ρ, y_w, b) as an approximate solution of Eq. (2)

In agreement with the observations presented before, a function $g(\rho, y_w, b)$ as solution of Eq. (2) must: (i) be defined for $\rho \geq \rho_{\min} = 1/y_w$ and $b \geq 0$, and (ii) increase monotonously with ρ, showing a horizontal asymptote at $g = 1$.

After testing several function types, we found that functions of form 1 − 1/exp(EXP), where EXP depends on ρ and MSD parameters and is null for $\rho = \rho_{\min}$ and increases with ρ, can be modeled well for the aim proposed. As $\rho_{\min} = 1/y_w$, the variable $z = \rho y_w$ will be sometimes used instead of ρ, so that the exponent EXP would contain a binomial $(z^{E(z,b)} - 1)$ as a factor, where $E(z, b)$ is a function to be found. After a number of trials, we focused on the following equation:

$$g(z,b) = 1 - \exp\left[2k\left(1 - z^{1/k(1+m\ln z)}\right)\Big/\exp b^2\right] \tag{5}$$

where k and m are functions of b the expressions of which must be found. One observes that g depends on two variables only, z and b, the variables ρ and y_w entering into the variable z.

The function in Eq. (5) has some target properties, namely:

I. It equals zero for $z = 1$ or $\rho = 1/y_w$;
II. It increases with z, thus with ρ, if the exponent of z is positive and decreases with z;
III. Another property, which is very important for applications, is that the function in Eq. (5) can be inverted and expressed in the form of $z = z(g, b)$ or $\rho = \rho(g, y_w, b)$.
IV. Finally, it can be easily seen that $\partial g/\partial z|_{z=1} = 2/\exp b^2$ that leads to

$$\partial g/\partial \rho|_{\rho=1/y_w} = \partial g/\partial z|_{z=1}\partial z/\partial \rho = 2y_w/\exp\left(b^2\right) = 2y_n \tag{6}$$

that is similar to Eq. (3d). Therefore, Eq. (5) follows well the ρ dependence characteristics of the gel fraction, both in gel point and for $\rho > \rho_{\min}$. A good matching of this function with the "exact" solution of Eq. (2) has been realized by introducing the parameters k and m as functions on the dispersity b. Their expressions

$$k(b) = 23.75/\left(1 + 33.82b^{2.46}\right) \quad \text{and} \tag{7a}$$

$$m(b) = -0.171 + 0.739b^2 - 0.275b^4 + 0.057b^6 \tag{7b}$$

are deduced in the Appendix. Therefore, the function proposed as a solution of Flory–Charlesby's equation has the expression:

$$g(z,b) = 1 - \exp\left\{2k(b)\left[1 - z^{1/k(b)[1+m(b)\ln z]}\right]\Big/\exp b^2\right\} \tag{8}$$

where $z = \rho y_w$ and the functions $k(b)$ and $m(b)$ are given in Eqs. (7a) and (7b), respectively.

2.4. Characteristics of g(z, b) function others than those in Section 2.3

V. By replacing z with the product ρy_w, one results the function $g(\rho, y_w, b)$. One observes in Fig. 1 that the curves g–ρ string well the numerical solution points of F–C equation for both L–K and W distributions. Visible differences between these curves and the “exact” solution points appear for $b > 1$ or $y_w/y_n > 2.7$, so that for rather molecularly disperse polymers.

VI. Inversability of $g(\rho, y_w, b)$. By solving Eq. (8) relative to z and then replacing z by ρy_w, the expression of the crosslinking density, ρ, as a function of g, y_w and b, is:

$$\rho(g, y_w, b) = y_w^{-1} r(g,b)^{k(b)/[1-k(b)m(b)\ \ln\ r(g,b)]} \tag{9}$$

where

$$r(g,b) = 1 - 0.5k(b)^{-1} \exp b^2 \ln(1-g) \tag{10}$$

with k (b) and m (b) given by Eq. (7). Expression (9) is especially useful for determination of ρ from gel fraction measurements. Such measurements can be carried out easier than those of swelling ratio or Young modulus or thermal extension.

How ρ changes with g and b is showed in Fig. 2 for the two types of log norm distributions, L–K and W. Normally, the curves $\rho(g, b)$ can be obtained from the curves $g(\rho, b)$ (Fig. 1) by a 90° rotation followed by a mirror reflection. One observes that the determination of ρ from g measurements is theoretically much more precise for $g < 0.7$ than for $g > 0.9$. Fig. 2 shows also that the curves corresponding to different b values intersect one another for both types of MSDs.

VII. The relative deviation of $\rho(g, y_w, b)$ function from the “exact” F–C equation solution was found for $y_0 = 1000$ and different b and g values to be between $+1.2$ and $-$ 0.2% for $b = 0$, between $+0.34$ and -0.5% for $0.1 \leq b \leq 0.8$, between -2 and 0.2% for $b = 1.0$, but may reach -5% for $b = 1.2$ and -9% for $b = 1.4$. Because the gel fraction is usually measured with errors not lower than about 5%, it can be said that the Eqs. (8) and (9) can be successfully used for polymers with $b \leq 1.2$ or $y_w/y_n < 4.2$.

VIII. Sometimes, the relationship (1), which is characteristic to molecularly monodisperse polymers, is also used to estimate the crosslink density from gel fraction measurements in the case of primary polydisperse polymers. As Fig. 3 shows, the relative error of using relationship (1) becomes unacceptably large when b and g are not small enough. For example, one can find that this error remains lower than 5% if $g < 0.6/(b \exp 2.5b)$.

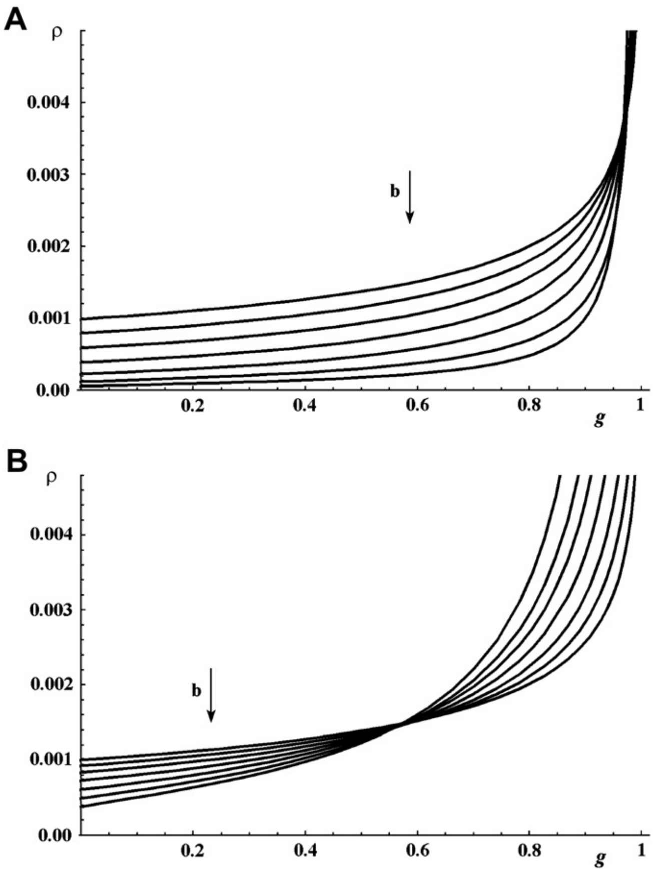

Fig. 2. Density of crosslinking, ρ, versus insoluble gel fraction, g, obtained using Eq. (9) for L–K (plots A) and W (plots B) log norm distributions, with $y_0 = 1000$ and various b values (0.1, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4, in the arrow direction).

3. Applications to crosslinked 1,2-polybutadiene

It is known that 1,2-polybutadiene (PB) is a rather easily crosslinkable polymer under free radical conditions due to the reactivity of the allyl and vinyl groups. There are many studies published about the crosslinking of this polymer [23]. The present study refers to its thermal crosslinking produced by two crosslinking agents, AIBN and ABC diazide, the purpose being to obtain information about the crosslinking yield and mechanism. Another goal was to correlate the crosslink density determined from gel fraction measurements and the temperature T_D for which the damping factor, tan D, where D is the stress–strain phase lag in DMA (Dynamic Mechanical Analysis), is maximum [24].

3.1. Experimental

3.1.1. Materials

1,2-Polybutadiene (PB) was used as it was kindly supplied by Japan Synthetic Rubber under the name JRS-RB820 and had the following characteristics: 1,2 unit content of 92%, predominantly syndiotactic, crystallinity of 25%, density of 0.906 g/cm^3, and 80 °C melting point. The molecular weight characteristics, namely an approximate log norm MSD with $y_w = 1700$ ($M_w = 91{,}800$ g/mole) and $b = 0.75$, were obtained by GPC in toluene, using polystyrene standards for calibration and the following Mark–Houwink–Sakurada parameters: (i) $K = 0.12$ ml/g and $\alpha = 0.71$ for polystyrene, and (ii) $K = 0.00009$ ml/g and $\alpha = 0.81$ for 1,2-polybutadiene [25]. AIBN and ABC diazide from Aldrich were purified by precipitation with petroleum ether from chloroform.

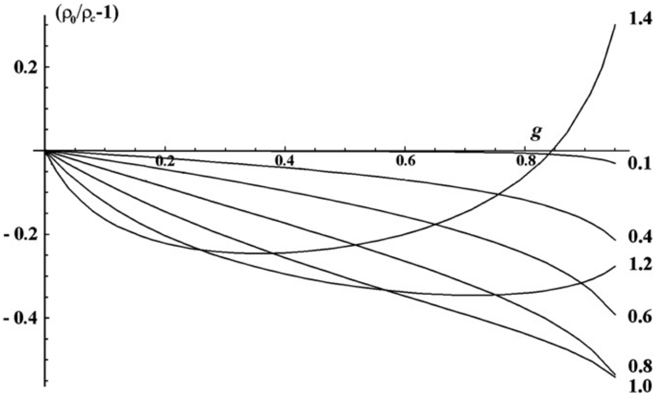

Fig. 3. Gel fraction dependence of the relative error $(\rho_0/\rho_c - 1)$ where ρ_0 and ρ_c are calculated with the Eqs. (1) and (9), respectively, considering $y_0 = y_w$. The numbers on the curves correspond to the b values.

3.1.2. Sample preparation and crosslinking

Blends of 1 g PB each with several AIBN concentrations (0.5, 1, 1.5, 2, 2.5 and 3% w/w) were prepared by mixing corresponding volumes of chloroform solutions of the two components. A similar procedure was used to obtain blends of PB with different ABC diazide concentrations (0.25, 0.5, 1, 2, 3.5 and 7% w/w). Tinuvin 622 (0.1%) from Ciba was used as antioxidant into each blend. As the density of crosslinking is a numerical fraction, it is indicated to give the primary composition of a blend as the ratio between the numbers of crosslinker molecules and butadiene units. Further on, such a ratio will be named crosslinker fraction and will be noted f_c. The values of f_c can be found knowing that 1% AIBN in PB corresponds to $f_c = 0.00325$ and 1% ABC in PB corresponds to $f_c = 0.00146$. The samples subjected to crosslinking were films of 0.2–0.3 mm thickness obtained by solution casting on Teflon support. The crosslinking process was performed by about 2 h heating in nitrogen atmosphere at 130–135 °C. FTIR-ATR spectroscopy was used to prove that the crosslinker decomposition was complete.

3.1.3. Characterization of crosslinked samples

The gel fraction was determined by weighing the sample before and after a 3 h Soxhlet extraction with chloroform. During extraction, the samples were separated between them by using individual stainless steel sieve baskets. The temperature dependence of damping factor (tan *D*) was recorded in tension mode on a Perkin–Elmer Diamond DMA apparatus at a heating rate of 2 K/min and a testing frequency of 1 Hz.

3.2. Characterization of the system PB-AIBN

The points (f_c, $10^3\rho$) in Fig. 4 were obtained from (f_c, g) experimental values by using Eq. (9) with $y_w = 1700$ and $b = 0.75$. It was found that a function fitted well on these points is

$$1000\rho(f_c) = 2.0962 \times 10^{-6} - 0.54298 f_c^{0.1} + 9.95 f_c^{0.3} - 10.285 f_c^{0.5} \qquad (11)$$

By means of this function it was possible to find, for example, the fraction of crosslinker corresponding to the gel point – a parameter difficult to be obtained experimentally. Hence, a value $f_c = 0.000683$ results by solving Eq. (11) for $\rho = 1/y_w = 1/1700$.

Fig. 4 presents also how the ratio ρ/f_c depends on f_c. One observes that this ratio, which is the crosslinking yield relative to the decomposed crosslinker, decreases rapidly with the concentration of crosslinker. Such a dependence shows that the consumption of AIBN radicals by recombination, which is a bimolecular reaction (Scheme 1a), is the more predominant relative to the crosslinking process (Scheme 1b) so as f_c is greater.

$$\textbf{AIBN} \xrightarrow{\Delta} 2\ \text{NC-}\dot{\text{C}}\text{(CH3)2} + \text{N2}$$

$$2\ \text{NC-}\dot{\text{C}}\text{(CH3)2} \longrightarrow \text{NC-C(CH3)2-C(CH3)2-CN} \qquad \text{(a)}$$

$$2\ \text{NC-}\dot{\text{C}}\text{(CH3)2} + 2\ \textbf{PB} \longrightarrow 2\ \text{NC-CH(CH3)2} + \textbf{PB-PB} \qquad \text{(b)}$$

Scheme 1.

The crosslinking mechanism with AIBN (Scheme 1) is based on the formation of macromolecular radicals by hydrogen atom extraction by AIBN radicals from the polymer chains [26]. The presence of the low molecular AIBN products resulting in reactions 1a and 1b (Scheme 1) was confirmed by their sharp signals at 1.38 ppm (singlet) and 1.32 ppm (doublet) in the ^{1}H NMR spectra of the extracted fractions of crosslinked samples. These products plasticize the crosslinked polymer leading to lowering of the values observed for T_D. As a result, a T_D rise of only 0.3 K was measured for a PB-AIBN sample with the gel fraction of about 0.6.

3.3. Characterization of the system PB-ABC

Unlike the crosslinking with AIBN, the thermolysis of diazides leads to nitrene biradicals that produce crosslinks by both hydrogen atom extraction and insertion into the C–H bonds of the polymer chains (Scheme 2). Unlike the system PB-AIBN, the low molecular thermolysis products of ABC diazide have stiff structures, hence their plasticization effect is expected to be low or absent. In order to obtain a good $T_D{-}\rho$ correlation, it is better to measure T_D on samples that contain all the reaction products. The extraction of soluble components from the samples leads to deformed samples, inadequate for accurate mechanical measurements. On the other side, a tendency of component separation was observed for samples with $f_c > 0.01$.

The gel fraction values measured for samples with different ABC concentrations are plotted as g curve in Fig. 5. One observes that g

$$\textbf{ABC} \xrightarrow{\Delta} \text{:N-aryl-N:} + 2\ \text{N2}$$

$$\text{:N-aryl-N:} + 4\ \textbf{PB} \longrightarrow \text{H2N-aryl-NH2} + 2\ \textbf{PB-PB} \qquad \text{(a)}$$

$$\text{:N-aryl-N:} + 2\ \textbf{PB} \longrightarrow \textbf{PB}\text{-NH-aryl-NH-}\textbf{PB} \qquad \text{(b)}$$

$$2\ \text{:N-aryl-N:} \longrightarrow \text{:N-aryl-N=N-aryl-N:} \longrightarrow \qquad \text{(c)}$$

Scheme 2.

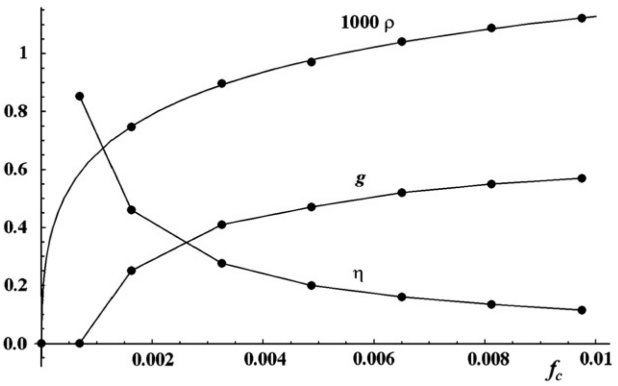

Fig. 4. Crosslinker fraction dependences of g (measured values), ρ (values calculated with Eq. (9) from corresponding g values), and crosslinking yield $\eta = \rho/f_c$ for crosslinked PB-AIBN samples.

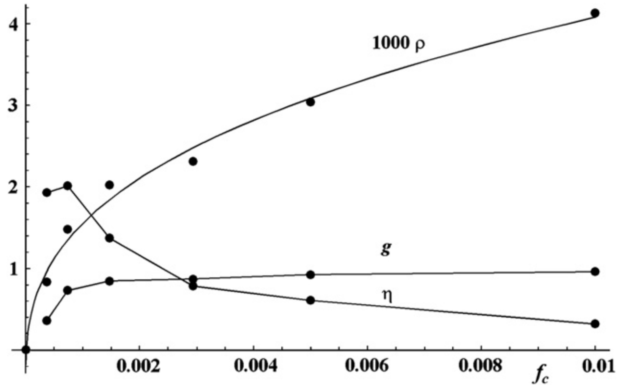

Fig. 5. Crosslinker fraction dependences of g (measured values), ρ (values calculated with Eq. (9) from corresponding g values), and crosslinking yield $\eta = \rho/f_c$ for crosslinked PB-ABC samples.

increases with f_c more rapidly than for PB-AIBN samples (Fig. 4), hence it proves that ABC is a more efficient crosslinker than AIBN. Like for the previous system, the corresponding values of the crosslink density were calculated using Eq. (9) and a function which fits well the points (f_c, ρ) was found to be

$$1000\rho(f_c) = -0.001503 - 1.7569 f_c^{0.1} + 17.1627 f_c^{0.3} + 9.7905 f_c^{0.5} \tag{12}$$

The value $f_c = 0.000145$ was calculated for the crosslinker fraction corresponding to the gel point.

Several interesting observations can be made from the plot ρ/f_c. As expected, the ABC diazide is a more efficient crosslinker than AIBN. Even more interesting, the crosslinking yield ρ/f_c value is close to 2 for much diluted blends, which means that the crosslinking process takes place mainly by hydrogen atom extraction (reaction 2a; Scheme 2). This fact is somewhat unexpected because the polymer crosslinking with aromatic diazides is usually attributed in the literature to the nitrene insertion (reaction 2b) [27]. An additional argument for PB crosslinking by the reaction 2a is that the ^{1}H NMR spectra of the soluble fractions of blends with $f_c < 0.001$ showed sharp signals that may be explained by formation of corresponding primary amines. That the ratio ρ/f_c still decreases to subunitary values when f_c increases is a consequence of the nitrene recombination (reaction 2c) and this reaction is also supported by the orange color of crosslinked samples, the intensity of which increases strongly with f_c.

3.3.1. *Influence of crosslinking on the molecular mobility*

The first studies about the increase of glass transition temperature, T_g, with crosslink density [28] as well as corresponding theoretical and empirical relations [29–31] have been reported fifty-sixty years ago. The reference used is the linear equation of Fox and Loshaek [29], although deviations from linearity have also been reported [30,31]. Later, Stutz et al. [32] have formulated a generalized theory for the T_g of uncrosslinked and crosslinked polymers. Nevertheless, all studies reported up to now are related to highly crosslinked systems ($\rho > 0.01$) of both types: networks formed by copolymerization (vinyl/divinyl copolymers, for example) and postsynthesis crosslinked polymers (rubbers, for examples) [32].

The samples presented before in this article are characterized by ρ values between 0.001 and 0.01 at $y_w = 1700$ and may be considered weakly crosslinked systems. Further on, the crosslink density dependence of the temperature T_D of these samples will be presented. We chose this parameter because it can be measured more accurately than, for example, the temperature values corresponding to inflection points in DSC and modulus DMA curves, which is an important requirement for weakly crosslinked samples. Of course, the value T_D is not identical with the values T_g determined from DSC or modulus DMA thermograms, which, in their turn, are dependent on the recording conditions as heating rate and testing frequency. Our supposition is that the difference $\Delta T_D = T_D - T_{D0}$, where T_{D0} characterizes the uncrosslinked polymer, is proportional with the difference ΔT_g induced by crosslinking.

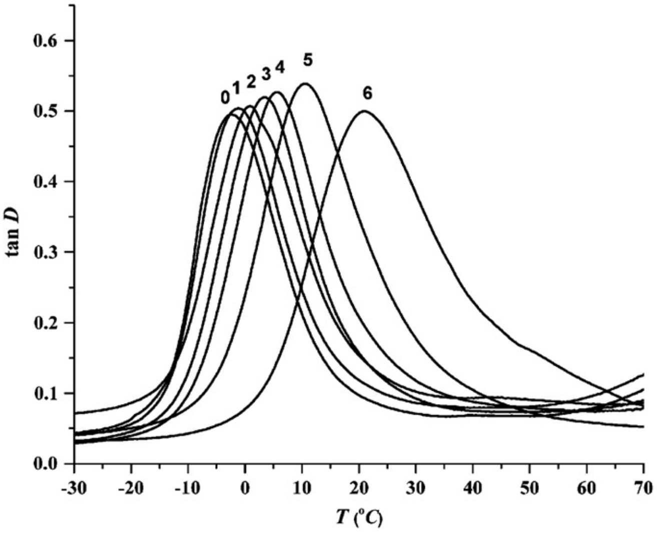

Fig. 6. DMA–tan *D* thermograms for PB-ABC samples with different crosslink densities: 0.0 (0), 0.00083 (1), 0.00148 (2), 0.0020 (3), 0.0023 (4), 0.0030 (5) and 0.0041 (6).

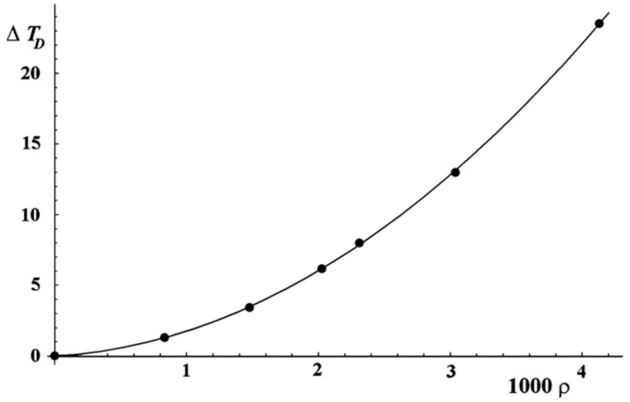

Fig. 7. Crosslink density dependence of $\Delta T_D = T_D - T_{D0}$ difference as experimental data (●) and $\Delta T_D = \rho\,(0.502 + 1.256\rho)$ plot (continuous line).

One observes in Fig. 6 that the thermograms tan *D* show a rather symmetrical bell shape for $\rho < 0.005$. Their maxima shift to higher temperature and broadened when ρ increases. The points (ρ, ΔT_D) plotted in Fig. 7 show a non-linear dependence. For example, these points stretch rather well on a second order curve,

$$\Delta T_D = \rho(0.502 + 1.256\rho) \tag{13}$$

Deviations from the linear dependence $\Delta T_g \sim \rho$ (Fox–Loshaek) have been reported even for strongly crosslinked polymers. In the case of weakly crosslinked systems, particularly around the gel point (one crosslink per molecule, on average), the molecular mobility is slowed down by at least two processes. One of them is the increase of chain length, the effect of which persists as long as the amount of chains non-included into the network is not negligible. The contribution of such a process to the glass transition temperature is given by the Flory–Fox's equation [33]. The other process affecting the molecular mobility is the shortening of chain segments between adjacent branching points, the ΔT_g of which being considered in the Fox–Loshaek's equation. As ΔT_D is assumed as correlated with ΔT_g, the two processes may determine a non-linear relation between T_D and ρ.

A DMA–tan *D* method of ρ determination is especially useful when *g* is nearly 1, because the sol–gel method then becomes too imprecise. A disadvantage of a DMA-based method is that relationships similar to Eq. (13) must be established for each crosslinking system studied.

4. Conclusions

Eq. (8) or (9) fits well the solution of Flory–Charlesby equation for crosslinked polymers having log norm primary MSD with $b \le 1.2$ or $y_w/y_n < 4.2$. These functions are especially useful in the case of postsynthesis crosslinked polymers, when the estimation of crosslink density from the reaction parameters is too difficult or not even possible. Eqs. (8) and (9) are rather mathematically tractable, being invertible and easily derivatized. Their superiority over empirical relationships like, for example, that of French [34]:

$$\rho = kg^2/(1-g) \tag{14}$$

which is considered one of the best, refers to at least two aspects. The first is taking into consideration the influence of molecular dispersity on the relationship between gel fraction and density of crosslinking. The second is the fact that functions (8) and (9) are general relationships between ρ and g, which depend only of MSD parameters. One can say that the functions in discussion have got elements of the primitive integral of the Flory–Charlesby's equation for log norm MSD.

As applied to 1,2-polybutadiene crosslinked with AIBN and ABC diazide, Eq. (9) allows to determine ρ from measurements of g and, by such a procedure, it was possible to obtain information about gel point, crosslinking yield and mechanism. It was found that the crosslinking yield decreases rapidly with crosslinker concentration for both crosslinkers and that ABC diazide is a more efficient crosslinker than AIBN. In addition, by analyzing the DMA–tan D curves for polybutadiene-ABC samples, it was found that the temperature T_D, for which the damping factor is maximum, increases with ρ following an approximate second order dependence. Quantitative correlations between ρ and ΔT_D can lead to a method of characterization of rubber vulcanizates, which is rather convenient because the measurements of T_D are precise and easily performed.

Other foreseen applications would be the ability to check and calibrate other methods of crosslinking determination, or to establish the effect of crosslinking density on some phenomena in polymers, such as the processes of mechanical, electrical or nuclear magnetic spin relaxations.

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Appendix

A1. Definitions of MSD parameters

N_i – the number of molecules build up of y_i mers.
$N_i y_i$ – the number of mers included in molecules containing y_i mers.
$\sum_i N_i y_i$ – the total number of mers in the sample.
$y_n = \sum_i N_i y_i / \sum_i N_i$ – the number average degree of polymerization or the number average of mers in one molecule.
$y_w = \sum_i N_i y_i^2 / \sum_i N_i y_i$ – the weight number degree of polymerization.
$y_z = \sum_i N_i y_i^3 / \sum_i N_i y_i^2$ – the z-average degree of polymerization.
$w(y_i) = N_i / \sum_i N_i$ – the fraction of molecules containing y_i mers of the total number of molecules in the sample.

Note: the limits of summation are from $y_{\min}$ to $y_{\max}$. As a rule, the distribution functions are normalized to the unit, i.e. $\sum_i w(y_i) = 1$.

A2. Continuous form expressions of MSD parameters

y– the number of mers in a certain molecule or the polymerization degree.
$w(y)$ – the distribution function or the number of molecules each containing y mers.
$w(y)\,\mathrm{d}y$ – the number of mers in the molecules with the degree of polymerization between y and $y + \mathrm{d}y$.
$w(y)\,\mathrm{d}y/y$ – the number of molecules each containing numbers of mers between y and $y + \mathrm{d}y$.
$y_n = \int w(y)\,\mathrm{d}y / \int [w(y)/y]\mathrm{d}y$ – the number average degree of polymerization.
$y_w = \int w(y) y\,\mathrm{d}y / \int w(y)\,\mathrm{d}y$ – the weight average degree of polymerization.

Note: the limits of integration are from $y_{\min}$ to $y_{\max}$. As a rule, the distribution functions are normalized to the unit, i.e. $\int w(y)\,\mathrm{d}y = 1$.

A3. Common MSD functions and average values of the degree of polymerization

Lausing–Kraemer (L–K) log norm distribution [35,36]:

$$w(y) = \left\{(2\pi)^{0.5} b y_0 \exp[0.5(\ln y/y_0)^2/b^2 + 0.5b^2]\right\}^{-1},$$
$$y_n = y_0 \exp\left(0.5b^2\right) \quad \text{and} \quad y_w = y_0 \exp\left(1.5b^2\right)$$

where y_0 is the most frequent degree of polymerization and b is the dispersity (a measure of the spread of the distribution).

Wesslau (W) log norm distribution [35,36]:

$$w(y) = \left\{(2\pi)^{0.5} b y \exp[0.5(\ln y/y_0)^2/b^2]\right\}^{-1},$$
$$y_n = y_0/\exp\left(0.5b^2\right) \quad \text{and} \quad y_w = y_0 \exp\left(0.5b^2\right)$$

where the most frequent degree of polymerization is $y_0 \exp(b^2)$ and b is the dispersity.

Tung-Weibull distribution [35]:

$$w(y) = r(s+1)y^3/\exp\left[r y^{(s+1)}\right],$$
$$y_n = 1/\left[r^{1/(s+1)}\Gamma[s/(s+1)]\right] \quad \text{and}$$
$$y_w = \Gamma[1/(s+1)]/\left[(s+1)r^{1/(s+1)}\right]$$

where r and s are variables without direct interpretation and $\Gamma(x)$ is the function gamma of the variable x.

A4. Expressions in and near the gel point

The gel point is the state where the insoluble gel fraction, g, begins to be non-zero. Near the gel point, where $\rho y_i g \ll 1$ and, consequently, $\exp(-\rho y_i g) \cong 1 - \rho y_i g + 0.5(\rho y_i g)^2$, Eq. (2′), which is the expression form given by Charlesby to the Flory's Eq. (2), leads to:

$$g = \rho g \sum_i N_i y_i^2 / \sum_i N_i y_i - 0.5(\rho g)^2 \sum_i N_i y_i^3 / \sum_i N_i y_i$$
$$\text{or} \quad 1 - \rho y_w + 0.5\rho^2 g y_w y_z = 0$$

from where Eq. (3) can be directly derived.

A5. Flory–Charlesby's equation written with distribution functions of continuous form

Using the definitions in A1 and A2, it results that $\sum_i N_i y_i$ must be replaced with $\int w(y)\,\mathrm{d}y$, $\sum_i N_i y_i (1-\rho g)^{y_i}$ with $\int w(y)(1-\rho g)^y\,\mathrm{d}y$, and $\sum_i N_i y_i \exp(-\rho g y_i)$ with $\int w(y)\exp(-\rho g y)\,\mathrm{d}y$. For normalized distribution functions, when $\int w(y)\,\mathrm{d}y = 1$, Eqs. (2) and (2′) take the expressions $g = 1 - \int w(y)(1-\rho g)^y\,\mathrm{d}y$ and $g = 1 - \int w(y)\exp(-\rho g y)\,\mathrm{d}y$, respectively.

A6. Finding the expressions of functions k(b) and m(b)

The method used was based on the transposition of Eq. (5) under the form:

$$(\ln z)/\ln\left[1 - 0.5k^{-1}\exp\left(b^2\right)\ln(1-g)\right] = k + km\ln z$$

and plotting of the left part of this new equation as function of $\ln z$ by using the values b, g and $z = \rho y_W$ obtained by the numerical solution of Eq. (2). For example, the case of L–K molecular weight distribution will be presented. To get the value of k corresponding to a certain b value, various values were given to k and the value that leads to the best linear plot was chosen. By using the least-squares fit operation, the following equations were found for the linear dependences chosen: $23.8296 - 4.1147\ln z$ for $b = 0.0$, $21.2973 - 3.5172\ln z$ for $b = 0.1$, $5.2269 - 0.30248\ln z$ for $b = 0.4$, $2.2386 - 0.14108\ln z$ for $b = 0.6$, $1.1535 + 0.23649\ln z$ for $b = 0.8$, $0.67244 + 0.24373\ln z$ for $b = 1.0$, $0.421783 + 0.22987\ln z$ for $b = 1.2$, and $0.266898 + 0.21533\ln z$ for $b = 1.4$.

Then, the expression (7a) of the function $k(b)$ was obtained by fit operation applied to the pairs of (b, k) values corresponding to the intersection points of the straight lines with the ordinate.

The next step was to use the best-squares fit operation to find the expression (7b) of the function $m(b)$ which best fits the pairs of (b, m) values, where m is the slope of the straight line that corresponds to a certain b value.

The method presented before to find the expressions of $k(b)$ and $m(b)$ functions for L–K distribution was repeated for W distribution and a rather good resemblance of functions $k(b)$ and $m(b)$ corresponding to the two log norm distributions was found.

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