The effect of butadiene and acrylonitrile components on the relaxation properties of butadiene-acrylonitrile copolymers

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The majority of relaxation transitions in poly(butadiene-co-acrylonitrile) that are observed above the glass transition temperature are connected with the butadiene component. The acrylonitrile component affects the glass transition temperature and the temperature of chemical decomposition of the polymer, and it leads also to the occurrence of the relaxation process connected with the mobility of local dipole-dipole cross bonds.

Der Einfluß der Butadien- und Acrylnitril-Komponenten auf das Relaxationsverhalten von Butadien-Acrylnitril-Copolymeren

Die Mehrzahl der Relaxationsübergänge in Poly(butadien-co-acrylnitril) oberhalb der Glasübergangstemperatur hängen mit dem Butadienanteil zusammen. Der Acrylnitrilanteil beeinflußt die Glasübergangstemperatur und die Temperatur der chemischen Zersetzung des Polymers. Er ist auch für das Auftreten des mit der Beweglichkeit lokaler Dipol-Dipol-Querbindungen zusammenhängen Relaxationsprozesses verantwortlich.

Влияние бутадиенового и акрилонитрильного компонентов на реалаксационные свойства бутадиенакрило-нитрильных сополимеров

Большинство релаксационных переходов в сополимерах бутадиена и акрилонитрила, наблюдаемых выше температуры стеклования, связано с бутадиеновым компонентом. Акрилонитрильный компонент оказывает влияние на температуру стеклования и температуру химического распада полимера, а также приводит к появления релаксационного процесса, связанного с подвижностью локальных диполь-дипольных попереч-ных связей.

1. Introduction

Copolymers are seldom characterized by a pure statistical distribution of units in the polymer chain [1]. Therefore the individuality of A and B units is supposed to appear in the relaxation processes in copolymers. The purpose of this paper is to ascertain the contribution of the butadiene and acrylo-nitrile units to the relaxation processes observed by means of relaxation spectrometry in butadiene-acrylonitrile copolymers.

2. Relaxation transitions in poly(butadiene-co-acrylonitrile)

Figure 1 presents the dependence of the glass transition temperature on the content of nitrile units. The glass transition temperature for polyacrylonitrile is taken from [2]. The other data are taken from various scientific papers [3]. It follows from Figure 1 that the dependence for T_g is of a non-linear character. Extrapolation of this dependence gives for the atactic polybutadiene the value $T_g = -55\,°C$, which is close to literature values ($T_g = -50\,°C$).

According to the data on stress relaxation for copolymers and atactic polybutadiene, above the glass transition temperature 13 different relaxation processes are observed. Two of them are chemical relaxation processes: δ_s is the process related to the decomposition of the chemical cross bonds in the rubber network, and δ_c is the process connected with the disintegration of weak C—C bonds in the polymer chains.

Just above T_g two relaxation processes are observed: μ_{pb} which is related to the decomposition of the physical nodes formed by the interaction of the —CH=CH$_2$ side groups of the butadiene links [1, 2], and π_s which is explained by the disintegration of the dipole-dipole (cross) bonds between the polymer segments with intramolecular chemically bound sulfur. Within the temperature range between these and the chemical relaxation processes further transitions are observed, to which, first and foremost, belongs the group of λ-transitions connected with the
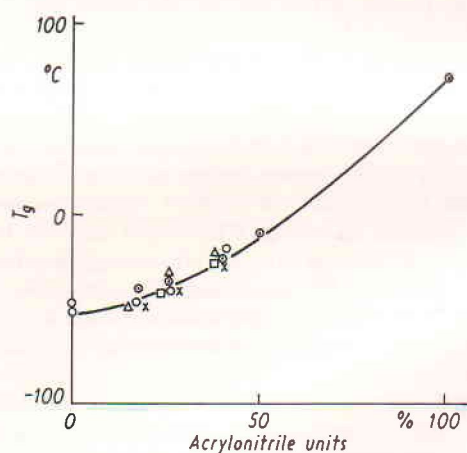

Fig. 1. Dependence of the glass transition temperature on the content of nitrile units in poly(butadiene-co-acrylonitrile)

decomposition of microvolume physical nodes of the molecular network. These nodes represent the associates of bound segments of various types with different life time [4—7]. Up to seven λ-transitions are observed for the investigated polymers.

The π_N process, specific for the butadiene-nitrile elasto-mers, was discovered in the studies [6, 8]. This process is related to the decomposition of dipole-dipole cross bonds formed by the polar CN-groups of the nitrile units of the copolymers. For polybutadiene this process is not observed.

3. Effect of butadiene and nitrile components on the relaxation transitions

Almost all relaxation transitions are observed in poly-butadiene as well as in its copolymers. It means that in the copolymers containing up to 50% nitrile units the butadiene
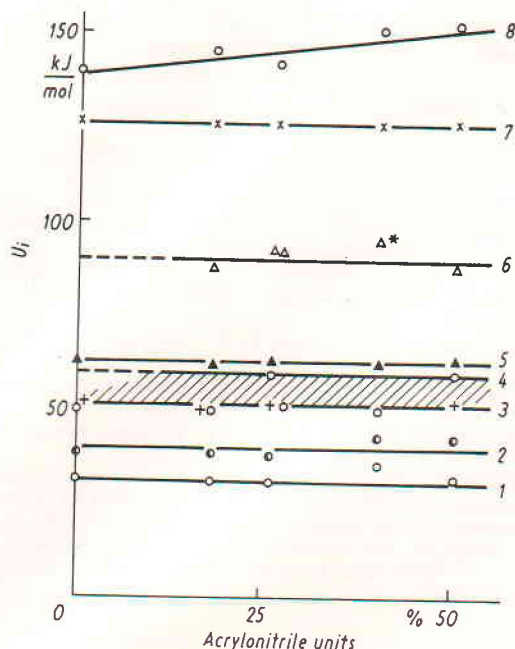
Fig. 2. Dependence of the activation energy of various relaxation processes on the content of nitrile units in the polymer chain. $1 - \beta$, $2 - \beta_1$, $3 - \mu_{pb}$, $4 - \lambda_i$, $5 - \pi_s$, $6 - \pi_N$, $7 - \delta_s$, $8 - \delta_c$

butadiene-nitrile elastomers is identical to the energy in polybutadiene (50 kJ/mol). According to our data for copolymers the activation energy equals to 60 kJ/mol. In other words, the copolymers are characterized by an activation energy U_i which lies within a certain region (Figure 2). This is connected with the fact that under different conditions of synthesis the individual nitrile units increasing the interaction energy of the bound segments in the associates are able to enter or not the butadiene segments of the polymer chain. The same situation is confirmed by the data in Figure 3. This figure hints that the factors of the Boltzmann-Arrhenius equation $\tau_i = B_i \exp (U_i/kT)$ for the corresponding relaxation transitions in the copolymers practically do not depend on the content of nitrile
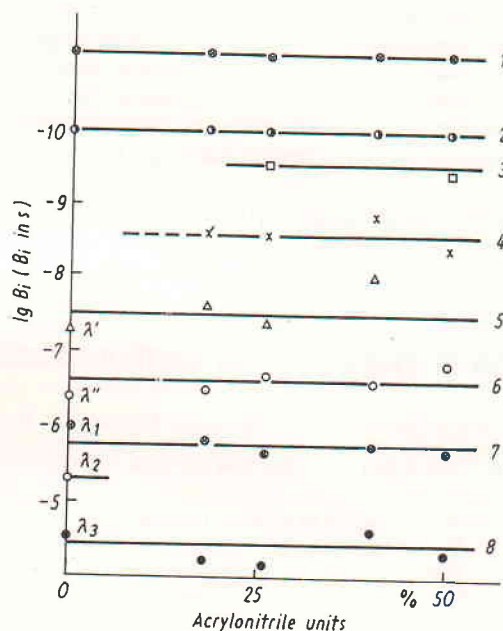
component plays an essential part in the relaxation phenomena. The π_s- and δ_s-relaxation processes are predetermined by the presence of the rubber network. For these processes only the part of the butadiene units is important, because the process of curing by adding of sulfur proceeds at the C=C double bonds.

Figure 2 illustrates the interdependence of the activation energies and the content of the nitrile units in the polymer chain for all relaxation processes.

The local physical nodes formed by the dipole-dipole bonds between the added sulfur, which is not involved in bridges, evidently have the same nature as in polybutadiene. Therefore the activation energy as well as the transition temperature of the π_s-relaxation process are identical for the homopolymer and the copolymers. As for the bridged sulfur which forms chemical nodes of the rubber network, the nature of the decomposition (δ_s-transition) and the activation energy (Figure 2) are also identical for polybutadiene and its copolymers.

The butadiene links are responsible for α- und β-relaxation transitions in the copolymers. One can see that the activation energy of β- and β_1-transitions for the copolymers is the same as for polybutadiene (Figure 2). On the whole, the glass transition (α-process) is defined by the butadiene units, not by the acrylonitrile units. Figure 1 shows that the glass transition temperature in the copolymers with the nitrile groups content up to 50% insignificantly increases (the glass transition temperature of polyacrylonitrile is $T_g = 72\,°C$). The effect of the nitrile units on the α-process is manifested in the gradual decrease of the segmental mobility due to the growth of the content of nitrile units.

The μ_{pb}-relaxation process is observed both for polybutadiene and for all investigated copolymers and characterized actually by the same activation energy. The effect of the nitrile units on λ-transitions is of a more complicated character. Thus, in the paper [8] for instance, it is shown that the activation energy of λ-processes in the

Fig. 3. Dependence of $\lg B_i$ on the content of nitrile units in the polymer chain. $1 - \pi_s$, $2 - \mu_{pb}$-relaxation transitions; 3 to $8 - \lambda$-transitions: $3 - \lambda'$, $4 - \lambda''$, $5 - \lambda'''$, $6 - \lambda_1$, $7 - \lambda_2$, $8 - \lambda_3$
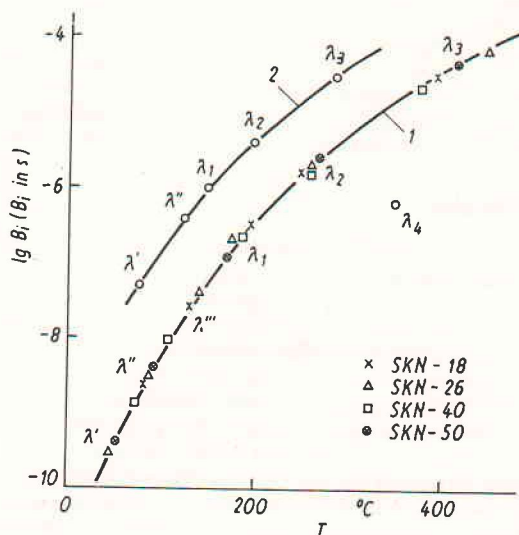

Fig. 4. Temperature dependence of $\lg B_i$ for the copolymers (1) and for polybutadiene (2). Temperatures correspond to the frequency $\nu = 1$ Hz

units, and for polybutadiene the values of B_i are considerably greater than for λ-transitions of the copolymers. The value of the factor B_i is directly related to the size of the microvolume of the physical nodes. In the copolymers, B_i is smaller due to the smaller size of the associates — the butadiene segments in the polymer chains of the copolymers are considerably smaller than in the macromolecules of homopolybutadiene.

The difference in the microstructure between the butadiene segments in the copolymers and in the chains of polybutadiene can be seen from the temperature dependence of $\lg B_i$ (Figure 4), where all butadiene-nitrile copolymers lie on one curve which differs from the curve for polybutadiene.

The acrylonitrile units are directly responsible for the so-called π_N-relaxation transition. This process is observed in the copolymers, and it becomes the more apparent the greater the content of nitrile units is. The activation energy of this process (Figure 2) does not actually depend on the content of nitrile units in the copolymers. This is understandable as the structural elements that are responsible for this process (dipole-dipole bonds) are the same for all butadiene-nitrile copolymers.

As Figure 2 shows, the activation energy of the δ_c-relaxation increases with the increase of the number of the nitrile units in the polymer chain. This means that the strength of the bonds depends on the microstructure and on the composition of the polymer chain.

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