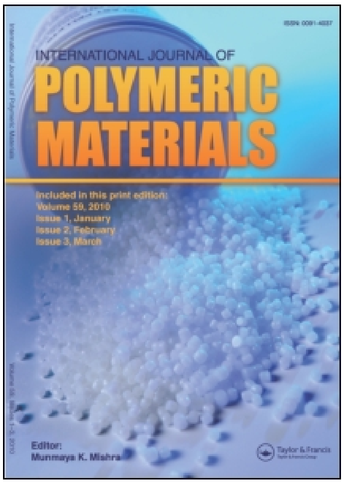

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Rheological Properties of Elastomers at Network Formation

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Changes of viscoelastic properties of polyisoprene (PI) in the process of crosslinking were studied. The obtained results were compared with kinetics of gel-fraction formation and crosslinking agent insertion. For systems with prolonged induction period of crosslinking good agreement in the change of viscosity, storage modulus and tan δ was noted. The appearance of the maximum on tan δ-vs-time curve correlates with flow cessation (gel-point). The increase of viscosity without the crosslinking agent insertion was noted before gel-point. It is related to increasing molecular mass of PI and can be expressed in terms of power law with the exponent equal to 5.6. After the gel-point sharp increase of storage modulus depending on the crosslinking system used was noted. At that moment overall network structure was formed and intensive insertion of crosslinking agents was observed. Change of viscoelastic characteristics of PI in crosslinking can be satisfactory described by the equation of a self-acceleration type.

KEY WORDS Elastomer compositions, polyisoprene, rheological properties, crosslinking, gel-point, network.

INTRODUCTION

The possibility to control the process of network structure formation in elastomers has a great importance for elastomer processing. Some works described the overall process of network formation from reactive oligomer compounds.[1-3] At the same time analogous data for high molecular elastomers are not sufficient. In some papers the rheological properties of filled and unfilled elastomers without crosslinking agents under capillary viscometry for technological purposes were studied.[4,5] The purpose of the present paper is to study by rheological methods the rheological behavior of model compositions on the base of cis-1,4-polyisoprene (PI) during crosslinking process.

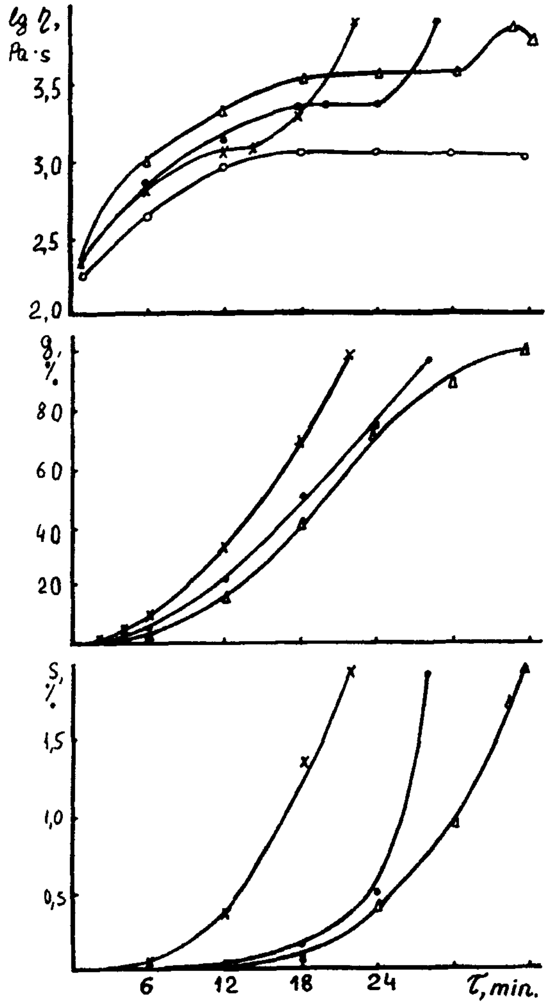

FIGURE 1 The change of viscosity (a), gel formation (b), contents of inserted sulphur (c) at crosslinking of PI (×, composition with sulphur/accelerator ratio = 2.5; •, composition with sulphur/accelerator ratio = 1.6; △, composition with sulphur/accelerator ratio = 2.5 and 0.1% wt. *N*-cyclohexylthiophtalimide; ○, PI without crosslinking agents).

MATERIALS

Model elastomer compositions were prepared on the conventional mills at 40–60°C. A commercial PI, zinc oxide, stearic acid, accelerators (*N*-Oxydiethylenebenzothiazole-2-sulphenamide, zinc diethyldithiocarbamate), sulphur and crosslinking inhibitor (*N*-cyclohexylthiophtalimide) was used in our experiment.

MEASUREMENTS

The viscometer "Rheomat-30" (from "Contraves" Co.) was used for viscosity of elastomer compositions determination at shear rates 0.571–2.65 s^{-1}. The gel-frac-

TABLE I

The molecular mass change of PI when heating

Time of heating of PI, min.	M_2[a]	M_w[b]	M_2[c]
0	240600	273300	242000
3	254300	293600	281300
8	269300	340000	292000
24	268400	338000	302000

[a] MM were determined through intrinsic viscosity in hexene.
[b] MM were determined by light-scattering method in hexene.
[c] MM were determined through intrinsic viscosity in toluene.

tion contents were determined by the sol-gel analysis method in toluene. The MM of PI were determined through intrinsic viscosity of polymer's solution in hexene and toluene at 25°C by the Bishof's viscometer. The combined sulphur contents were obtained by Shonigger's method.[6] The MM of PI by light-scattering method were determined on "Sofica" nefelometer in hexene at vertical polarized light (λ_0 = 5460 Å, 25°C). The dynamical characteristics of elastomer compositions (storage modulus, loss modulus, tan δ) were obtained by TBA-methods[7] at ~1 Hz.

RESULTS AND DISCUSSION

For systems with prolonged induction period of crosslinking, increase in viscosity without crosslinking agent (sulphur) insertion was noted (Figure 1a). Increase in viscosity for pure PI observed is connected with the changes of polymer structure under experimental conditions. The MM of polymer increases in this case (Table I). The process of MM growth can be described by a power law with a power dependency of 5.6 (the gel-content at this moment was equal to 5–30%, dependent on crosslinking systems composition—sulphur/accelerator ratio). Unusually high power dependence (universal value is a 3.5) may be connected with branched structure formation in PI.[8]

Good agreement was noted for investigated compositions in the change of viscosity, storage modulus and tan δ (Figure 2). The peaks in tan δ-vs-time curve were found in the region proceeding the increase in storage modulus curve. When comparing viscometric data with tan δ change, it was noted that the maximum of the latter correlates with the moment of flow cessation. It allows us to identify it as a gel-point.[9]

A sharp increase of storage modulus was noted after gel-point. At that moment overall network structure was formed and intensive insertion of crosslinking agent was observed (Figure 1).

When using crosslinking systems of high activity (without induction period), the rate of crosslinking increases sharply and experimental determination of induction period becomes impossible. The possibility to observe the change of rheological characteristics during the whole crosslinking process in this case appeared only

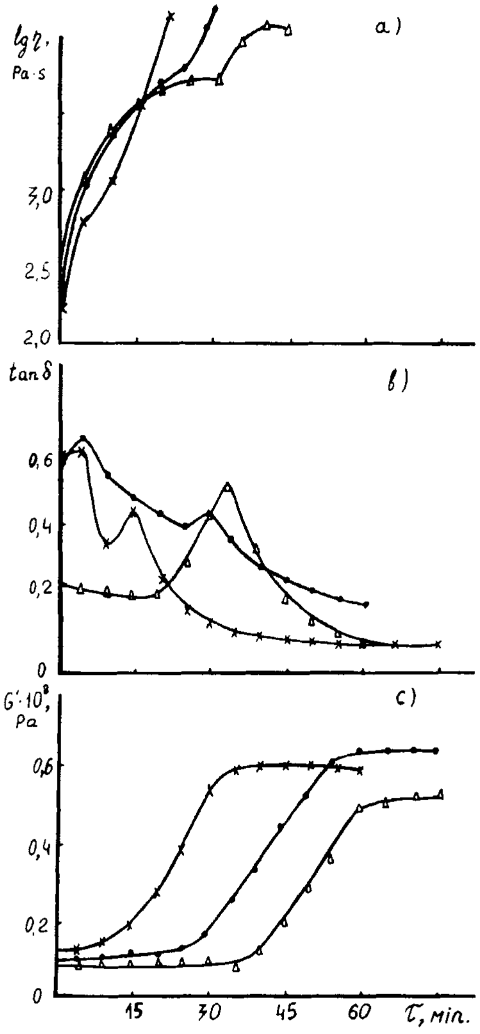

FIGURE 2 The change of viscosity (a), tan δ (b) and storage modulus (c) at crosslinking of PI. The symbols are the same as for Figure 1.

when a special inhibitor (*N*-cyclohexilthiophtalimide) was added and the temperature of the process changed to 120°C (Figure 3). The short time of induction period for system with zinc diethyldithiocarbamate does not allow to determine it experimentally. Thus, it was found that three main rheological effects are typical for all systems under investigation: increase of viscosity during induction period connected with the growth of polymer molecular mass, existence of induction period on the $G'(t)$ function and appearance of the tan δ maximum.

On the basis of experimental results the "rheological" measure of conversion (β) was determined:

$$\beta = \frac{G' - G'_0}{G'_\infty - G'_0}$$

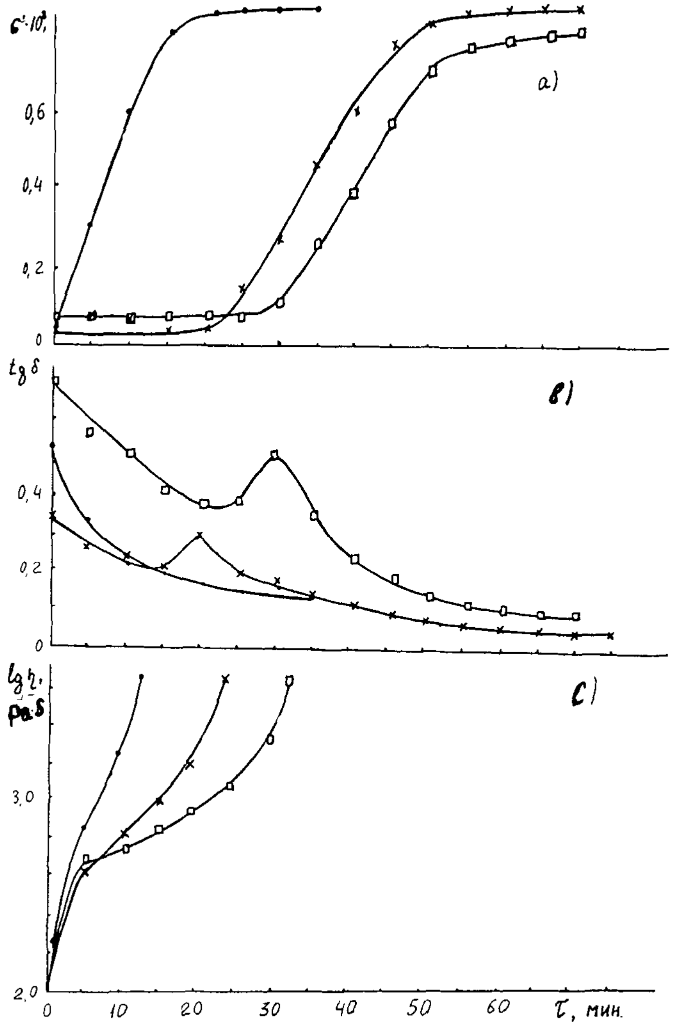

FIGURE 3 The change of storage modulus (a), tan δ (b) and viscosity (c) at crosslinking of PI (●, composition with accelerator of high activity (zinc diethyldithiocarbamate); ×, composition the same and 0.5% wt. *N*-cyclohexylthiophtalimide added; □, composition the same with additional 0.5% wt. *N*-cyclohexylthiophtalimide added).

where G' is the current value of storage modulus, G'_0 is the initial value of storage modulus, G'_∞ is the maximum of storage modulus at crosslinking. The shape of the $\beta(t)$ curves proves that the PI crosslinking process in isothermal conditions can be satisfactorily described by an equation of self-acceleration type:

$$\frac{d\beta}{dt} = k(1 - \beta)(1 + c\beta)$$

where β is "rheological" measure of conversion, t is time, k is constant of reaction rate, which is equal to crosslinking rate at $\beta \to 0$, c is constant connected with the self-acceleration effect.

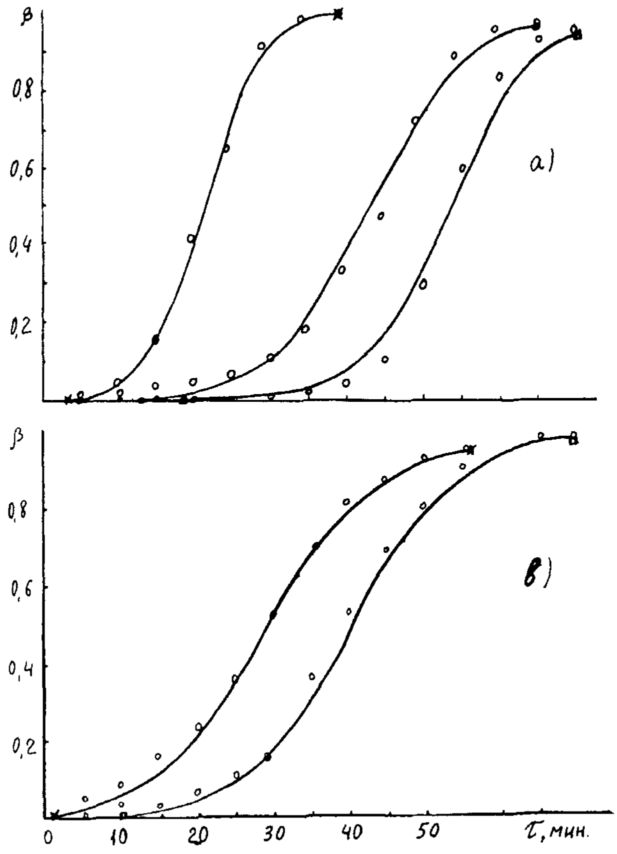

FIGURE 4 Rheological "measure" of convertion for systems as Figure 1(a) and for two latter systems as Figure 3(b). The points are experimental data and the lines are theoretical data.

Experimental and theoretical curves $\beta(t)$ show a good agreement between them (Figure 4). It justifies a choice of this equation for the correct description of elastomer compositions on the basis of PI at crosslinking.

The presented results prove the idea of identity of physical-chemical processes, which determines the network formation.[10] Peculiarities of this structure formation are connected with the stages of formation of reactive products which lead to autocatalysis of crosslinking reactions. These systems can be different in nature.

CONCLUSIONS

Rheokinetical methods of investigation of crosslinking processes in elastomers allow to determine the gel-point position and to control the process of network structure formation: from the appearance of discrete fragments of network structure and their transformation to overall network system. By this method we can describe the changes of viscoelastic characteristics by a simple self-acceleration type equation. Moreover, this description qualitatively agrees with ideas about chemical processes of elastomer crosslinking.

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