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Gelation Process

Synthesis of Networks in Solution

1. Influence of the Gelation on the Crosslink Kinetics

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SUMMARY

The kinetics of the solution crosslink process of polybutadiene is studied using a bistriazolinedione as crosslink agent. Beyond the gel point strong deviations from the pre-gel kinetics are observed due to the hindered translational diffusion in the gel.

INTRODUCTION

Networks obtained by crosslinking in solution have found widespread applications to test the predictions of the theories of rubber elasticity (1,2).
While in networks starting from endfunctionalized prepolymers only low extensions could be achieved, networks obtained by the EN-reaction of 4,4'-methylen-bis-(1,4-phenylene)-di-1,2,4-triazoline-3,5-dione (structure A in fig.1) with polymers containing allylic protons*) show high reversible extensability (3). This method has been used to synthesize networks of deuterated polybutadiene to investigate the deformation behaviour by ^{2}H-NMR (4).
In addition the gelation process itself is of certain interest. From theories about the behaviour near the gelation threshold it turns out, that in the case of solution crosslinking the critical conversion depends strongly on the polymer concentration (5,6,7). Especially an interrelation between the concentration where the polymer coils overlapp and the critical conversion where the gelation sets in, is predicted. In this paper the first results on the kinetics of the gelation process starting from anionically synthesized polybutadiene are reported.

KINETIC SCHEME

The crosslink process is represented by the reaction scheme

$$A + D \xrightarrow{k_1'} B \qquad [1a]$$

$$B + D \xrightarrow{k_2'} C \qquad [2a] \quad ,$$

where A,B,C are the structures shown in fig.1. D represents the doublebonds with allylic protons in the polymer chain.

*)EPDM rubber,containing biscyclopentadiene as ene-component can not be crosslinked by A, because the remaining allylic proton is in a bridgehead position and thus not available.

In the following the concentration of doublebonds is kept high compared with the number of crosslinks introduced ($\sim 100:1$). In this case the reaction scheme simplifies to

$$A \xrightarrow{k_1} B \qquad [1b]$$

$$B \xrightarrow{k_2} C \ . \qquad [2b]$$

The process can be represented by a series of pseudo-1. order reactions. The corresponding differential equations are

$$\frac{d\,c_A}{dt} = -\,k_1 \cdot c_A \qquad [3]$$

$$\frac{d\,c_B}{dt} = k_1 \cdot c_A - k_2 \cdot c_B \ , \qquad [4]$$

In fig.2 the UV-spectra of structures corresponding to A,B and C are shown. As model for B the Phenyl-1,2,4-triazoline-3,5-dione (structure P in fig.1) is used. Not shown is the main absorption at about 290 nm which appears in all three structures. A and B (=P) have an additional small maximum corresponding to the n$\longrightarrow\pi^*$ -absorption of the triazoline-dione-ring (8). The position of this maximum as well as the reactivity versus doublebonds depends on the solvent.

The extinction coefficients corresponding to A,B,C measured in THF at 527 nm (298 K) are listed in table 1. The absorption of C can be neglected up to conversions of 90%.For even higher conversions the small absorption of the product (C) must be taken into account.

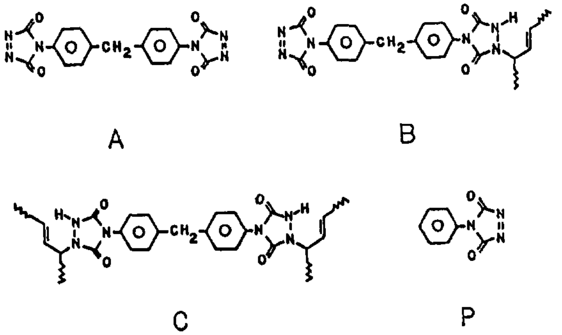

Fig.1: structures of the crosslink agent (A), the intermediate product (B), the final crosslink (C), the monofunctional model (P)

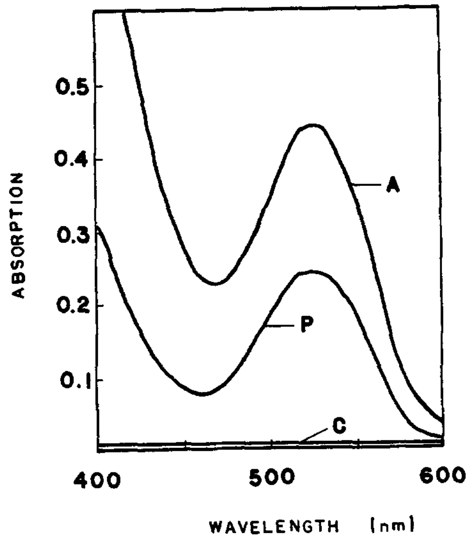

Fig.2: UV-spectra of the structures A,P,C (see fig.1) at the same molar concentration (1.5 mmol/l) in THF at 298 K

From the measurement of the absorption at 527 nm the total absorption of A and B is obtained. Using equations 3 and 4 with $f_1 = \varepsilon_B/\varepsilon_A$ the total change of the absorption is

$$\frac{d\,a_t}{dt} = \frac{d\,a_A}{dt} + \frac{d\,a_B}{dt} = (f_1 - 1)\cdot k_1 \cdot a_A - k_2 \cdot a_B \quad . \qquad [5]$$

Integration using for the initial absorption $a^o = a^o_A$ gives

$$a_t = a^o_A \cdot [\, e^{-k_1 t} + f_1 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})] \quad , \qquad [6]$$

where $a_t = a_A + a_B$ is the total absorption neglecting a_C.

To describe the reaction for conversions higher than 90% the small absorption of C must be taken into account. As conversion ρ of our reaction the fraction of C formed is defined by

$$\rho = \frac{c_C}{c_C^m} = \frac{c_C}{c_A^o} \quad , \quad \text{where } c_C^m \text{ is the concentration of C after total conversion.} \qquad [7]$$

This is written in terms of the absorption by

$$\rho = \frac{a_A^o + (1/f_1 - 1)\cdot a_A - 1/f_1\cdot a_t}{a_A^o} \qquad [8]$$

The absorption of C is given by

$$a_C = \rho\cdot f_2\cdot a_A^o \qquad \text{where } f_2 = \varepsilon_C/\varepsilon_A \qquad [9]$$

and the total absorption for high conversions is given by the sum of the absorptions of eq.6 and 9. The absorption a_t in eq.8 again is only the sum of a_A and a_B. Only if k_1 and k_2 are known, a_t can be calculated according to eq.6.

If only k_2 is known, the conversion and thus a_t can be determined by an iterative procedure: first a conversion is calculated based on the measured absorption according to eq.8. From this value a_C is calculated (eq.9). Then the measured absorption is reduced for a_C and a slightly higher conversion is calculated (eq.8), corresponding to a higher a_C. After 4 to 5 cycles a constant value for the conversion is obtained. To this conversion corresponds an absorption ($a_A + a_B$) which is the measured absorption reduced for the absorption of the product.

EXPERIMENTAL

The polybutadiene (M = 60000, 94% 1,4-structures) was prepared according to common anionic techniques using cyclohexane as solvent and n-butyllithium as initiator. The polymer as well as the polymer solutions in THF were stabilized adding about 1 wt.-% of 2,5-di-tert.-butyl-p-cresol. The crosslink agent A and the onefunctional model compound P were synthesized according to literature prescriptions (9).

All kinetic experiments were carried out in dried degased THF. The solutions of the triazoline-diones were freshly prepared. Cyclohexene was used as obtained from fractionated destillation. 2 ml aliquotes of the solutions of the enophilic reagent and the olefinic compound were mixed in UV-cuvettes and the absorbance was measured at 527 nm in a ZEISS PM2A-spectrometer. The sampleholder was thermostated to +/- 0.3 K. To estimate the activation parameters, measurements at 298,308 and 318 K have been carried out.

RESULTS AND DISCUSSION

MODELL REACTION WITH A LOW MOLECULAR WEIGHT OLEFIN

In fig.3 the reaction of A and P with a low molecular weight olefin (cyclohexene) is shown. The ratio of double bonds to triazoline-dione-groups is approximately the same as for the polymer case reported below.

Up to high conversions, the reaction of P with cyclohexene follows a pseudo-1.order reaction (straight line in a ln(a)/t - plot). This reaction is a model for eq. 2b with fixed initial concentration of B.

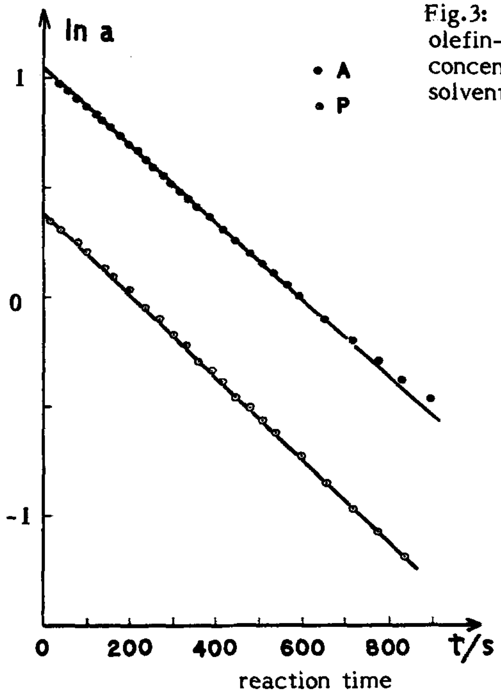

Fig.3: reaction of A and P with cyclohexene;
olefin-concentration: 1,98 mol/l
concentration of enophilic agent: 0.0093 mol/l
solvent: THF, 35°C

The reaction of A with the low molecular weigth olefin shows the same behaviour. In addition both straight lines have the same slope according to a similar reaction rate constant, but according to eq.6 the reaction of A with doublebonds should show a more complex behaviour. The observed simplified behaviour can be understood taking into account that the probability of a reaction of A is twice as high as the reaction of P (corresponding to B), so k_1 should be twice k_2 . Using in addition $f_1 = 0.5$ (table 1) then eq.5 and 6 reduces for this special case to the equation for a simple first order reaction with k_2 as proportionality factor

$$\frac{d\,a_t}{dt} = -k_2 \cdot a_t \quad . \qquad [10]$$

REACTION WITH POLYBUTADIENE

To study the influence of the gelation on the crosslink kinetics, polybutadiene with narrow molecular weight distribution has been used. The main problem in the case of the polybutadiene is the large number of loops formed (3).

In fig.4 the experimental data, reduced for a_C (according to the iterative procedure described above) for a series of different polymer concentrations are shown.

At low conversions the behaviour is the same as in the low molecular olefin case. From the slope k_2 can be determined according to eq.10. The data for measurements differing in polymer- and crosslink agent concentration are listed in table 2. The rate constant k_2' (obtained by dividing k_2 by the polymer concentration is 0.005 $\mathrm{l.mol^{-1}}$ at 298 K. In addition from measurements at 308 and 318 K the activation enthalpy $\Delta H^{\#} = 33$ kJ/mol is calculated. This value is considerably higher than for the DIELS-ALDER-reaction of the triazoline-dione-system with dienes (9). The activation entropy ($\Delta S\#$ = -177 E.U.) is very low, according to a highly ordered transition state.

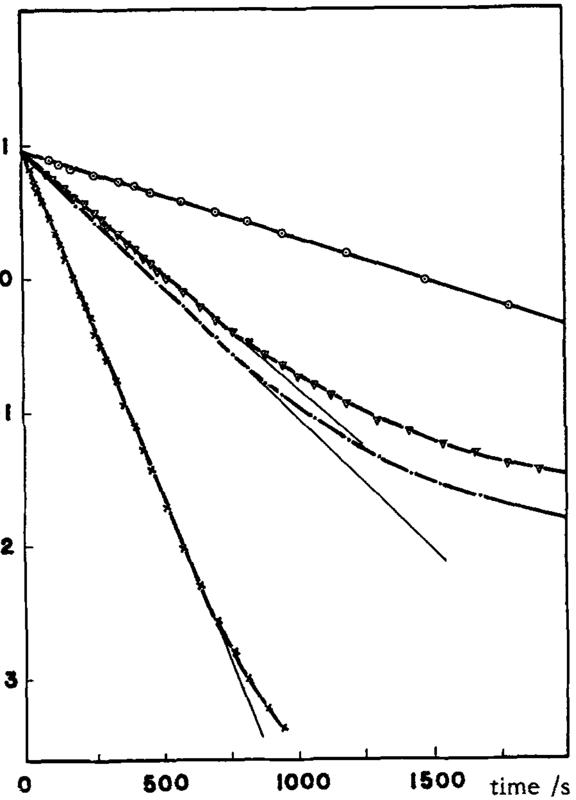

Fig.4: Measured absorption for the reaction of A (c_A^o = 0.0092 mol/l; 527 nm; THF; 298 K) with various polybutadiene concentrations; the concentrations are given in mole double-bonds/l; × = 0.925 • = 0.4625 ▽ = 0.324 o = 0.185

Table 1: UV-VIS-spectroscopic data

structure	extinction coefficient		
A	298 +/- 10	$l\ mol^{-1}cm^{-1}$	
B	150 +/- 10	$l\ mol^{-1}cm^{-1}$	f_1= 0, 5 +/- 0,02
C	8 +/- 3	$l\ mol^{-1}cm^{-1}$	f_2= 0,02 +/-0,01

For polymer concentrations below 0.5 wt.% no gel is formed for the concentration of A used in this study. In these systems the viscosity increased according to the formation of large but finite clusters. For higher polymer concentrations a strong departure from the linear behaviour results. All these systems

Table 2: Reaction conditions and obtained rate constants for the initial part for the crosslink reaction in THF

polymer concentration (wt.-%)	polymer concentration (mol/l doublebonds)	crosslink agent (mol/l)	temperature K	k_2 s^{-1}	k'_2 $l\ mol^{-1}s^{-1}$
5	0,925	0,0047	298	0,00463	0,005
2,5	0,463	0,0047	298	0,00242	0,0053
5	0,974	0,0092	298	0,00486	0,0049
5	0,925	0,0023	298	0,00403	0,0044
2,5	0,463	0,0092	298	0,002	0, 0043
2,5	0,463	0,0023	298	0,00227	0,0049
1,75	0,324	0,0092	298	0,00168	0,0052
1	0,185	0,0092	298	0,001	0,0054
2,5	0,463	0,0047	308	0,0038	0,0082
5	0,925	0,0047	308	0,0077	0,0083
2,5	0,463	0,0047	318	0,0081	0,017
5	0,925	0,0047	318	0,0122	0,0132

show gelation. Assuming that the reaction scheme (eq.1 and 2) does not change, this behaviour can only be explained by a time dependence of the 'rate constant' k_2^* . The first step of the reaction, involving the reaction of a highly mobile low molecular weight compound with the polymer will not be affected by the gelation.

The second step in the crosslink reaction involves a reaction of two polymers or of two separated parts of the same polymer. This reaction appears to become slower after the gelation threshold. For the highest polymer concentration the deviation again is smaller. Here a hindrance of the translational diffusion does not cause a drastic reduction of the reaction rate because of the increased number of doublebonds available.

The effective reaction rate constant k_2^* will depend on the network density. To keep k_2 as a system constant a retardation function R is defined

$$k_2^* = k_2 \cdot R(t) \qquad , \qquad [11]$$

This function is available from the experimental data according to

$$R(t) = -\frac{1/k_2 \cdot d\, a_t/dt + a_A^o \cdot e^{-2k_2 t}}{a_t - a_A^o \cdot e^{-2k_2 t}} \qquad , \quad [12]$$

More interesting than the time dependence of R(t) is the variation of this function with the conversion, because these plots directly allow the comparison of measurements performed under different conditions.

In fig.5 the retardation functions for the data of fig.4 are shown. For low conversions the reaction behaves like in the cyclohexene case, i.e. $R(\rho) = 1$. Then the situation as described above comes out more clearly. For the highest and the lowest polymer concentrations the deviations from the simple behaviour start at higher conversions. In fig.6 the influence of the crosslink agent concentration on the retardation function is shown for constant polymer concentration.

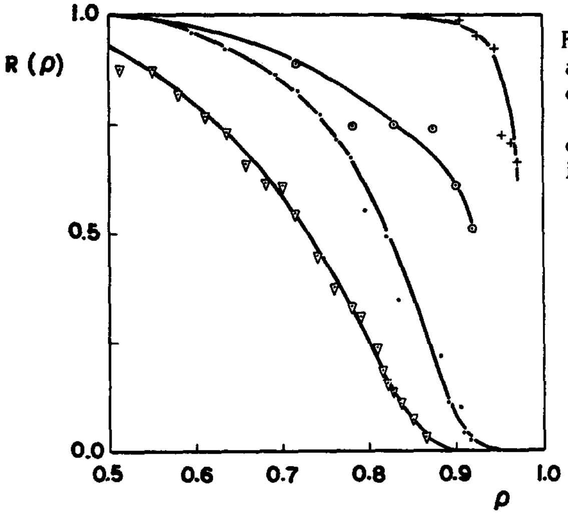

Fig.5: Retardation function as a function of the conversion; concentration of A: 0.0092 mol/l; THF, 298 K; double bond concentrations in mole doublebonds/l:

× = 0.925 • = 0.4625
▽ = 0.324 ○ = 0.185

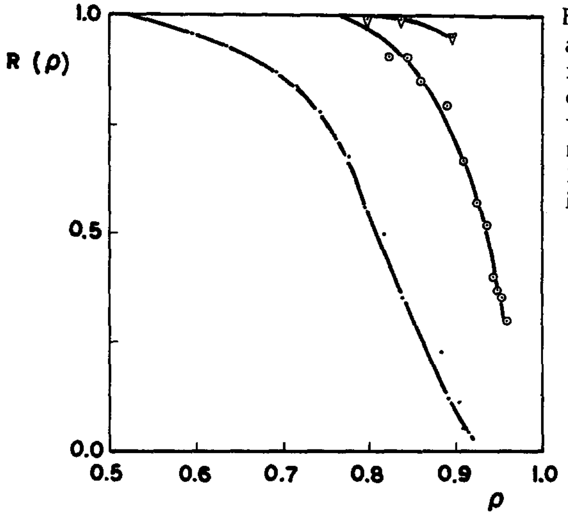

Fig.6: Retardation function as a function of conversion for various crosslink agent concentrations; polymer concentration = 2.5 wt.-% = 0.4625 mole doublebonds/l; THF, 298 K; concentration of A in mmol/l:

• = 9.2 ○ = 4.7 ▽ = 2.3

For the lowest concentration of A no gelation occurs. The deviation of R(ρ from 1 is small and within experimental error. With increasing concentration of A the deviation shifts to lower conversion as gelation does.

CONCLUSIONS

The kinetic results show that gelation has a strong influence on the crosslink reaction of polymers in semidilute solution. The deviations from the kinetic behaviour at higher conversions are correlated to the gelation. This effect can be attributed qualitatively to the hindered translational diffusion of polymer segments in the gel. This hindrance will increase with increasing crosslink density. According to earlier results (3) the number of loops introduced during the crosslink process is large. In a system with a lower amount of doublebonds like in butyl rubber the deviations should be more pronounced. These experiments are carried out presently. The next step to a proper understanding of the gelation process involves a theoretical description of the translational diffusion as a function of the gelation process.

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REFERENCES

(1) CANDAU S., BASTIDE J., DELSANTI M., Adv.Polym.Sci. 44, 27 (1982)
(2) BASTIDE J., PICOT C., CANDAU S., J.Macromol.Sci.,Phys. B19, 13 (1981)
(3) STADLER R., MALDANER JACOBI M., GRONSKI W., Makromol.Chem., R.C. 4, 129 (1983)
(4) GRONSKI W., STADLER R., MALDANER JACOBI M., Macromolecules (1984), in press
(5) DUSEK K., Polymer Bull. 1, 523 (1979)
(6) DE GENNES P.G., J.Physique 38, L-355 (1977)
(7) DAOUD M., J.Physique 40, L-201 (1979)
(8) BUTLER G.B., GRADY WILLIAMS A., J.Polym.Sci.,Polym.Chem.Ed. 17, 1117 (1979)
(9) COOKSON R.C., GUPTE S.S., STEVENS J.D.R., WATTS C.T., Org.Synthesis 51, 121 (1971)

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