Crosslinking of OH-functional polystyrenes through urethane bridges: kinetics of the three-dimensional addition reaction between hydroxyethyl functions and isocyanate groups of crosslinker

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We have reported in a previous paper the synthesis and features of two kinds of functional polystyrene precursors that lead through a gelation process to a three-dimensional network. This paper deals with an experimental kinetic study of the addition reaction between hydroxyl functions belonging to the polymer and isocyanate functions of the crosslinker. The reaction follows a simple second-order kinetics until an extent of reaction of 75%. The gel point is reached at the extent of 85%. Below the gel point a characteristic time τ is introduced for each reaction. It is found that all the gelling systems used in our studies exhibit the same rate constant.

(Keywords: polystyrene; networks; urethane links; kinetics; gelation)

INTRODUCTION

Model networks have been the subject of many theoretical and experimental investigations[1–6]. The aim of such studies is to understand network formation and to explain some of the properties of the final crosslinked material. It is well known[7] that these properties depend strongly on the preparation conditions and the history of the pregel region. However, before investigating the structure and the mechanical properties of the gel, a thorough preliminary chemical study of its formation is necessary, as many parameters play a role in the synthesis of these materials. Such knowledge can then allow an optimization of the gelation process.

The present paper deals with a kinetic study of the formation of urethane links, which lead the system to a crosslinked material. To describe the chemical kinetics of the network formation, we used Fourier-transform infra-red (*FT*-i.r.) spectroscopy, which is a very efficient tool for such a study. A chemical reaction may be followed from its onset to final conversion, even when a network is formed. The only prerequisite is the existence of a characteristic absorption peak that follows a well known law in a defined range of concentration and may be related accurately to the actual monomer content of the reaction medium. In the present case, the system follows the Beer–Lambert law. Thus, we have applied this method to investigate the kinetics of formation of a polystyrene network by the reaction of a polymer precursor (PS) fitted with hydroxyethyl functions and a pluriisocyanate (DRF or MDI; see below). We first checked that *FT*-i.r. spectroscopy is an appropriate method for such a system. It allows a better understanding of the chemical mechanism of the reaction between the hydroxyl functions and the isocyanate groups, and allows one to establish the order of the reaction in a defined region of the gelation process.

EXPERIMENTAL

Materials

Two kinds of polymer precursors of the same chemical nature were used in this study: linear α,ω-dihydroxyethylpolystyrenes (PS1, PS2 and PS3) and polystyrenes carrying pendent hydroxyethyl groups (PSA and PSB). The synthesis and characterization of these polymer precursors were described in detail in a previous paper[8]. In *Table 1* are gathered their principal characteristics.

Two crosslinking agents were used. The first one was a triisocyanate: tris(4-isocyanato)phenylthiophosphate (DRF) provided by Bayer in methylene chloride solution. The solvent was removed under reduced pressure and the remaining white solid dissolved in dry benzene and freeze-dried, yielding a white powder, which was stored under argon. The second was a diisocyanate: bis(4-isocyanato)phenylmethane (MDI) provided by Dow Chemical as a white solid, and used without further purification. The diazobicyclooctane catalyst (DABCO, Aldrich) was used as received. Crosslinking reactions were carried out in dry tetrahydrofuran (THF).

Stoichiometry

The stoichiometric ratio r, which characterizes the PS precursor/crosslinker systems, is defined as the initial ratio of alcohol to isocyanate groups. To fix this ratio, the functionalities of both the precursor polymer and the

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Table 1 Characteristics of the prepolymer precursor chains and experimental conditions used. τ is the characteristic time. Values are determined from the slope of the linear part of the function $1/(1-p)$ *versus* time t below the gel point. C_p is the prepolymer precursor concentration. C_c is the catalyst concentration. $\bar{M}_w$ and $\bar{M}_n$ are the weight-average and the number-average molecular weight ($g\,mol^{-1}$) determined by size exclusion chromatography. The nomenclature used to characterize the precursor samples and the experimental conditions appears in the figures

Samples	Nomenclature	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Functionality	C_p (% by weight)	C_c ($10^{-3}\,mol\,l^{-1}$)	τ (min)
PS1	P5/2/27/2.2	5500	5700	1.03	1.98	27	2.07	24.4
PS2	P10/2/15/3.8	10000	10200	1.02	1.98	15	3.77	29.2
PS2	P10/2/27/2.2	10000	10200	1.02	1.98	27	2.24	33.4
PS2	P10/2/35/1.3	10000	10200	1.02	1.98	35	1.32	49.5
PS3	P15/2/27/2.8	15200	15500	1.02	1.97	27	2.75	44.4
PSA	P60/8/27/2.4	59000	61000	1.03	8.10	27	2.44	44.7
PSA	P60/8/15/11.6	59000	61000	1.03	8.10	15	11.61	58.8
PSB	P60/4/27/4.5	58200	60200	1.03	4.20	27	4.50	51.2

crosslinking agent have to be known. The functionalities of the PS precursors were determined with good accuracy by u.v. spectrometry as described elsewhere[8]. Thus in the case of the difunctional polymers the value found was 1.98, very close to the theoretical value. The 'grafted' polystyrene precursors have a functionality of 8.1 (for the PSA sample) and 4.2 (for the PSB sample). The functionality of the crosslinkers, already checked in earlier investigations, is 3 for the DRF and 2 for the MDI, as indicated by the supplier[9]. The stoichiometric ratio can be calculated directly from the number of reactive groups present in the components.

Sample preparation

We have investigated the chemical kinetics of two types of gelling systems: the addition reaction of α,ω-dihydroxyethyl-terminated linear PS chains and tris(4-isocyanato)-phenylthiophosphate (PS/DRF) in the presence of diazobicyclooctane (DABCO) as a catalyst (the end-linking method, see *Figure 1*); and the crosslinking of a grafted hydroxyethyl PS with bis(4-isocyanato)phenylmethane (PS/MDI) in the presence of the same catalyst by a side-chain reaction (see *Figure 2*). The two antagonist functions react according to a simple addition reaction, yielding in both cases the same interchain link, which is a stable urethane group. The samples were prepared at 25°C under anhydrous argon by first dissolving the polystyrene prepolymer in anhydrous THF at a 27% concentration by weight. Then the catalyst was added at a 0.1% concentration by weight with respect to the prepolymer precursor. The crosslinker was added to the mixture in stoichiometric amounts. After mixing the reagents, the preparation was injected into an infra-red cell. The final products were colourless and transparent. All the experimental conditions are given in *Table 1*.

FT-i.r. measurements

The reaction mixture was injected into an infra-red cell formed by two NaCl salt plates. The path length was checked by a polytetrafluoroethylene spacer within the 20–25 μm range in order to prevent the strong isocyanate absorption band from being out of scale. This thin section also ensured isothermal conditions throughout the reaction. The cell was placed in a thermostatic device where the temperature was measured by means of a thermocouple placed directly between the salt plates. Isothermal conditions were regulated by a temperature controller within ±0.5°C.

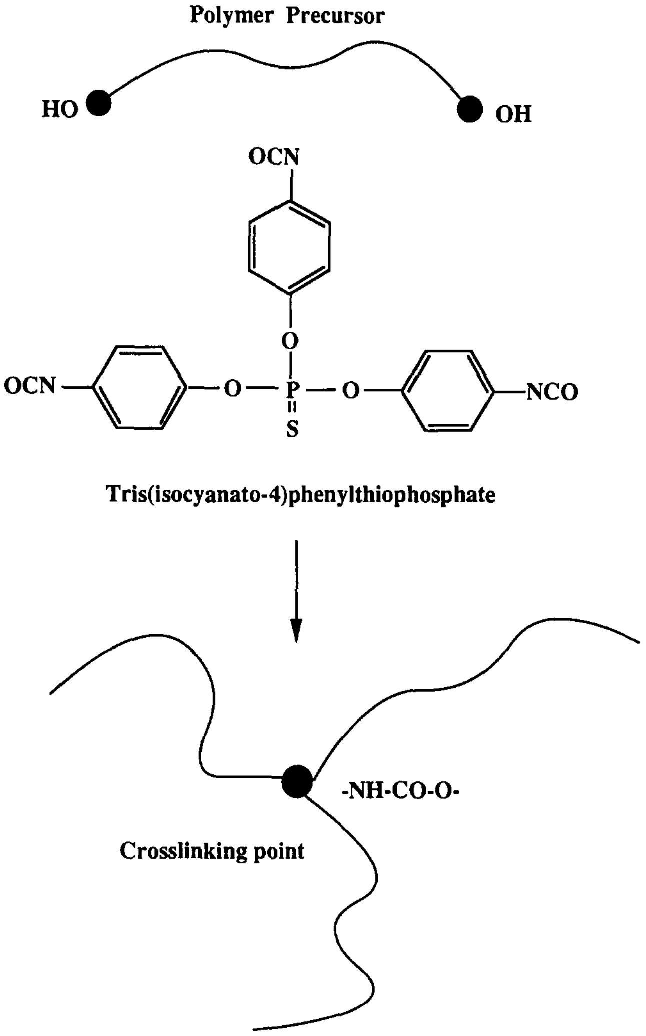


Figure 1 End-linking reaction for the model network. The junction is a trifunctional crosslinking point

The kinetics of the addition reaction was followed by *FT*-i.r. spectroscopy. Transmission spectra were obtained using a Nicolet 60SX Fourier-transform spectrometer by averaging 32 scans with a 2 cm^{-1} resolution, and one spectrum was recorded every 5 min during the gelation process. The characteristic isocyanate absorption band of the crosslinker at the wavenumber of 2273 cm^{-1} (*Figure 3a*) shows a gradual decrease, due to the

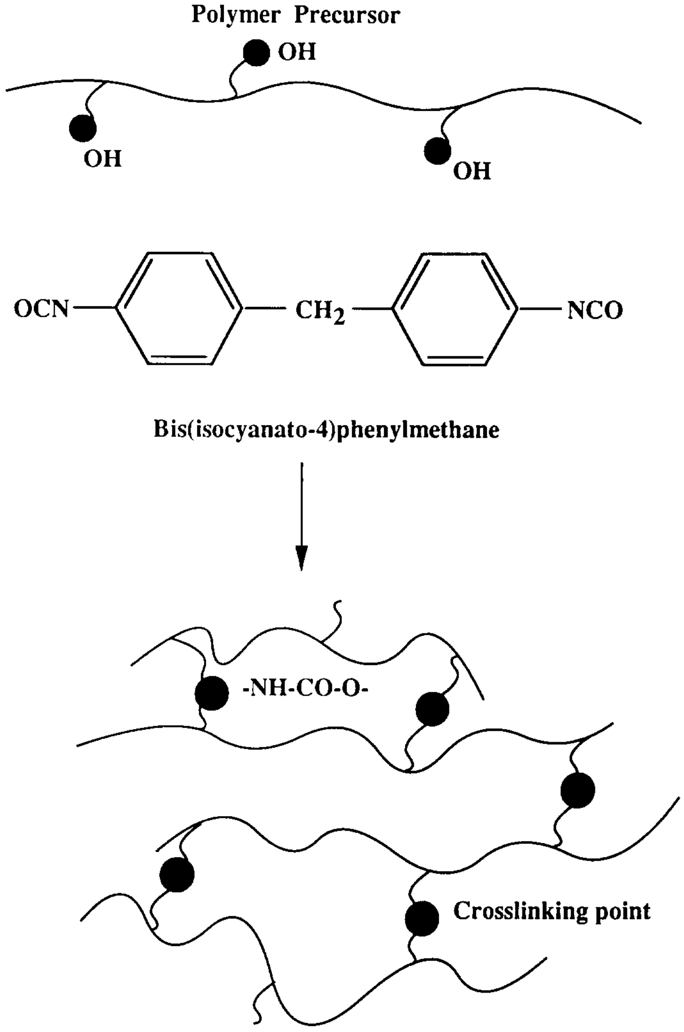


Figure 2 Side-chain reaction for the statistical network. The junction is a tetrafunctional crosslinking point

consumption of the latter as the gelation process proceeds, and can be used to monitor the extent of the reaction.

The absorption data are related to the extent of reaction by the Beer–Lambert law. The reaction conversion was calculated from the change of the normalized absorbance of the isocyanate peak as a function of time. For each experimental point, the following equation defines the extent of reaction p at a time t of the gelation process:

$$p=(A_0-A)/A_0$$

where A_0 is the NCO peak area of the unreacted reaction medium and A the peak area corresponding to subsequent reaction times. The integrated intensity under the broad peak at 795 cm^{-1} (see *Figure 3b*) remains constant throughout the course of the reaction, and its value was used as an internal standard of calibration for the isocyanate peak. In the same spectrum we observe the evolution of the C=O band at 1731 cm^{-1} (stretching vibration) and of the N–H band at 1544 cm^{-1} (deformation vibration), which are characteristic of a urethane linkage (see *Figure 3c*).

The absorbance for each experimental reading fluctuates by approximately 0.5% from one measurement to another, which corresponds to the expected accuracy of the *FT*-i.r. measurement in the conversion range considered here. The recorded kinetics of the reacting functional polystyrenes are shown in *Figures 4* and *5*, where we have plotted the conversion p as a function of time t. The reaction is very fast at the beginning, and an extent of reaction of 50% is reached after 30 min. At longer times the addition reaction slows down and the extent of reaction tends towards a limit. From this value on we suppose that chain coupling is more and more difficult. The kinetics of the addition reaction leading to a gel was followed up to a conversion of the order of 93%.

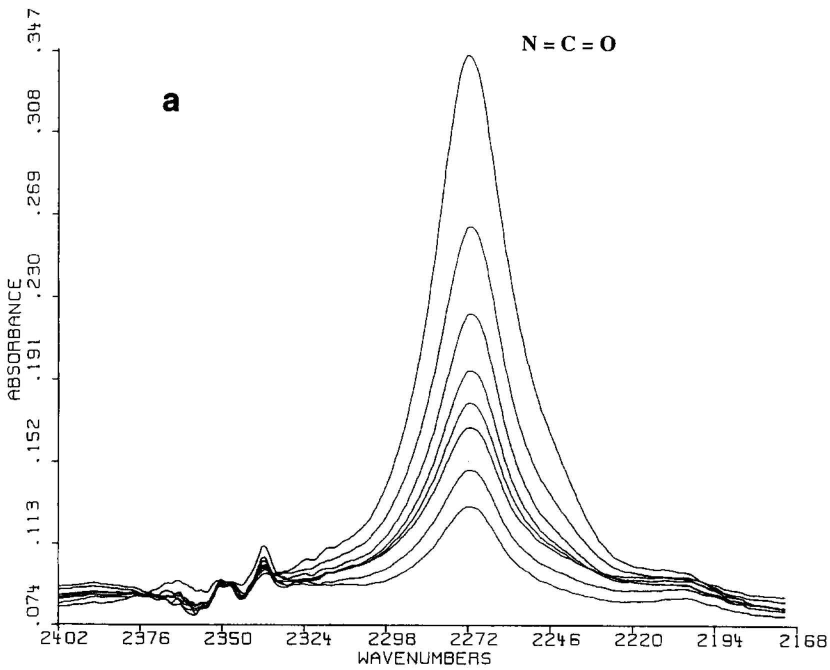


Figure 3 (a) Typical i.r. spectra showing the gradual decrease of the isocyanate groups. (b) Typical i.r. spectrum of the hydroxyethyl PS/crosslinker system during the crosslinking process. (c) Typical i.r. spectra showing the progressive appearance of the urethane links

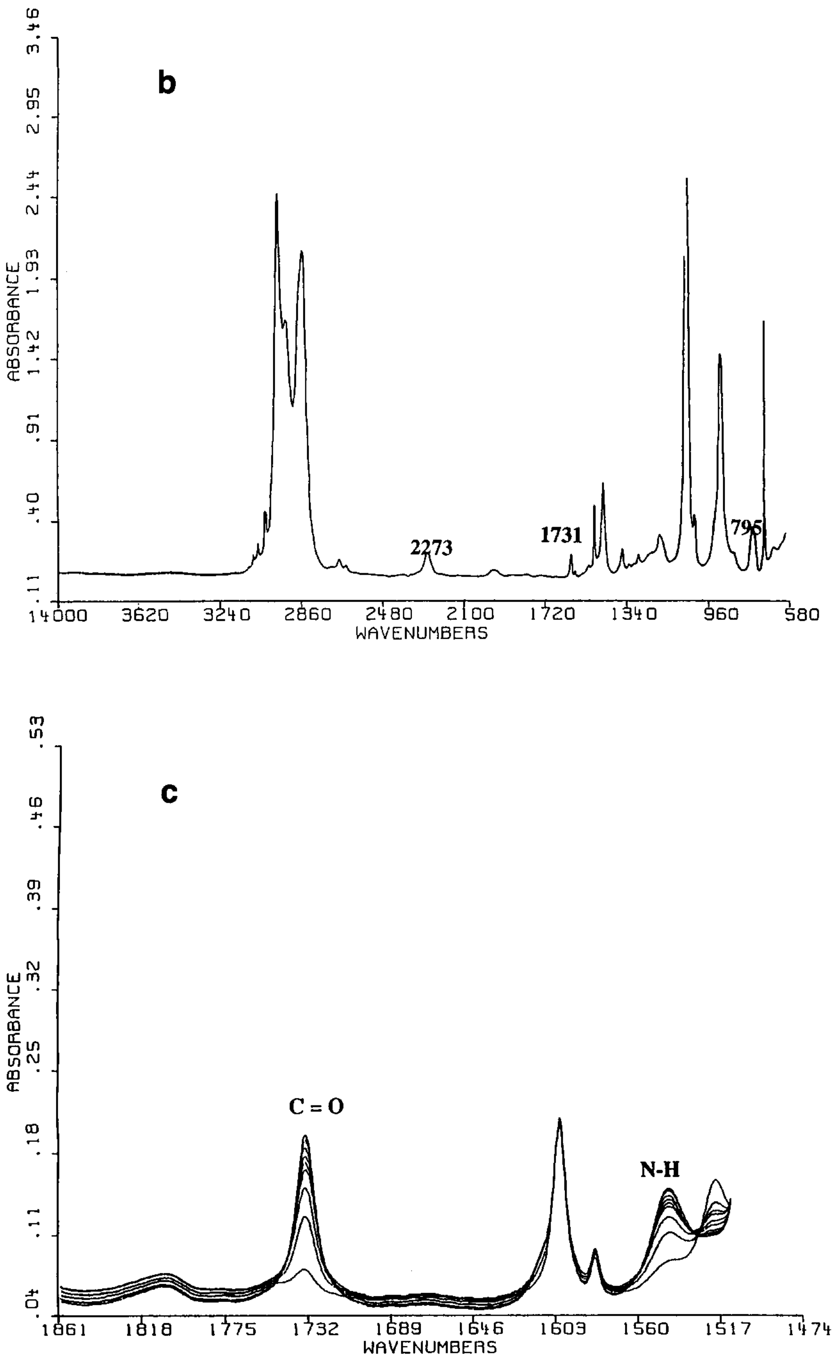


Figure 3 *continued*

RESULTS AND DISCUSSION

Concentration effects on the kinetics of the addition reaction

To check whether the concentration of the medium has an influence on the kinetics of the addition reaction, we have carried out some experiments with the difunctional PS of mass 10000 g mol^{-1} and the statistically grafted PS of mass 61 000 g mol^{-1} and functionality 8. We have considered three concentrations: 15%, 27% and 35% by weight. The results obtained from *FT*-i.r. experiments are shown in *Figure 5*, where the extent of reaction is plotted as a function of time *t* of the gelation process. These plots show that, at the beginning of the reaction, the rate of the addition reaction is highest for the system with the lowest concentration in polymer precursor. But when the conversion increases, the reaction rate slows down. An explanation of this behaviour will be given in the next section.

Kinetics in the pregel region

Prediction of a simple order reaction. Let us consider a system containing particles of two species A and B. These particles diffuse and upon colliding form an inert species C. In a reaction medium the reagents are in permanent motion. Since the reaction implies collisions between the reacting species, mobility is an important factor. The latter depends on the viscosity of the medium. In our particular system we have macromolecular reagents, small crosslinking molecules and increasing viscosity. Thus the diffusion mechanism becomes a predominant factor, which determines the kinetics of the reaction. Such systems are considered to undergo a

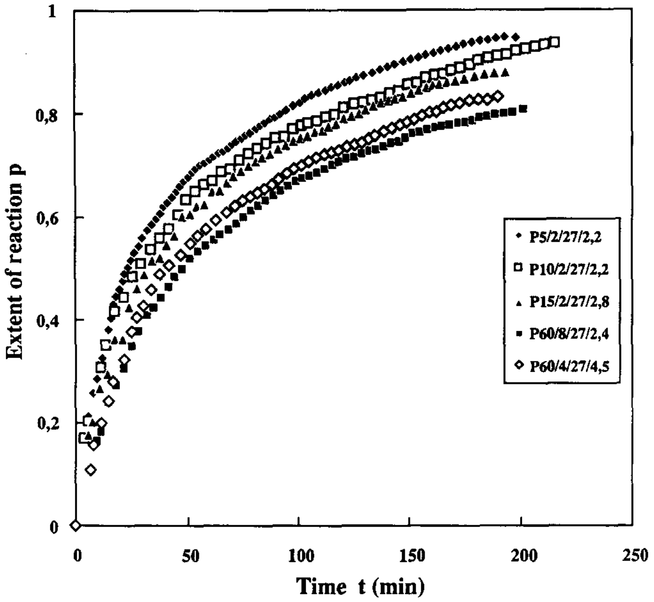


Figure 4 Extent of reaction p *versus* time t. Quantitative effect of the gelation process of the difunctional PS/DRF and 'grafted' PS/MDI systems (see *Table 1*)

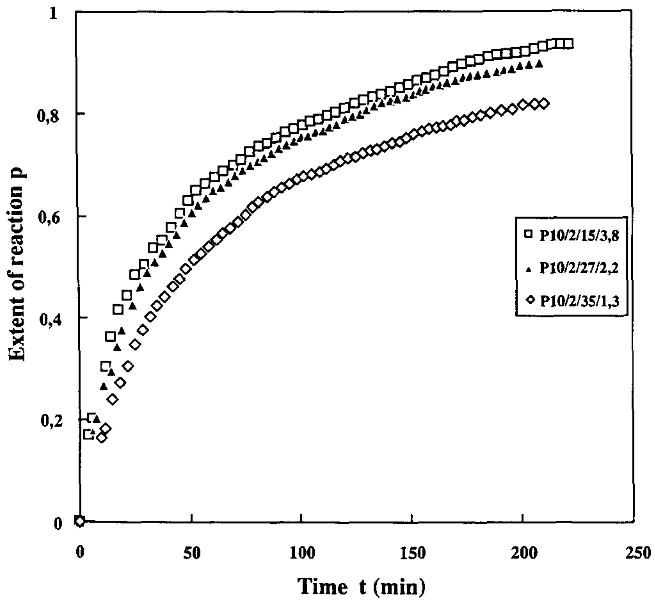


Figure 5 Influence of the precursor concentration on the kinetics of the addition reaction for the gelling system PS2/DRF

diffusion-limited process in a disordered medium. This two-species collision process is symbolically represented by:

$$A+B \rightarrow C \quad \text{with a reaction rate constant } k$$

In the mean-field limit[10–13], i.e. the reaction-limited case, the kinetics are described by the simple rate equations for the concentrations $C_A(t)$ of A particles and $C_B(t)$ of B particles at time t:

$$\frac{dC_A(t)}{dt}=\frac{dC_B(t)}{dt}=-kC_A(t)C_B(t)$$

In the special case of equal concentrations at initial time, $C_A(0)=C_B(0)$, the solution of the above differential equation is an algebraic decay:

$$C_A(t)=\left(kt+\frac{1}{C_A(0)}\right)^{-1}$$

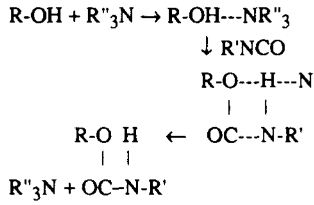
which is the mean-field prediction for the decay of concentration of the species A *versus* time.

The addition reaction of the systems PS/DRF and PS/MDI was carried out at a constant temperature of 25°C. In the absence of any side-reaction, the variation of the NCO concentration can be considered to be due only to the reaction between hydroxyl and isocyanate groups according to the following equation:

$$\text{R–OH}+\text{R}'\text{–NCO} \rightarrow \text{R–O–CO–NH–R}'$$

In this case a stable urethane function is formed. This reaction can exhibit a second-order behaviour as predicted by the mean-field limit. The plot of $1/(1-p)$ *versus* time t obtained from *FT*-i.r. measurements on the isocyanate absorption in the reaction of hydroxyethyl PS with DRF is shown in *Figure 6*. The same behaviour is observed with the PS/MDI system represented in the same figure. The analysis of this plot shows that obviously the reaction cannot be described by simple second-order kinetics.

In the presence of a catalyst like a tertiary amine, the reaction scheme of the addition reaction is given by:



Thus as suggested by the above reaction mechanism, the amine catalyst is not in direct contact with the isocyanate group. The amine forms an intermediate with the hydroxyl function when the latter reacts with the isocyanate group. The intermediate compound rearranges to yield a

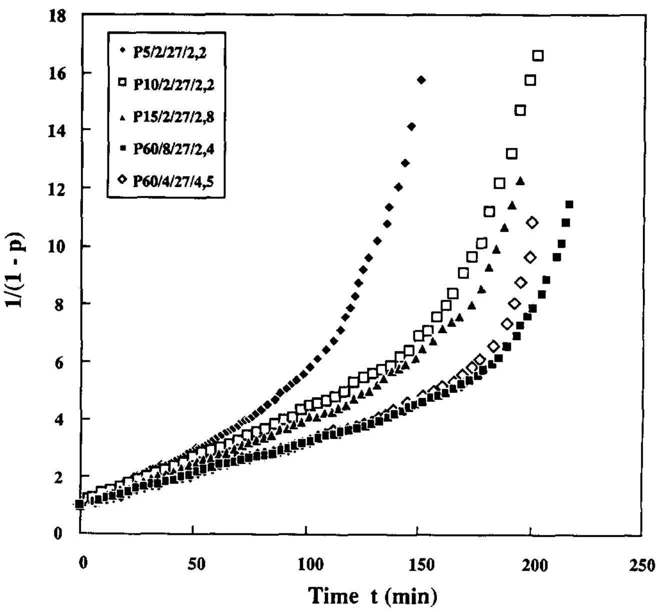


Figure 6 Variation of the ratio $1/(1-p)$ as a function of time t

urethane function. In this scheme, and provided the respective concentrations of NCO and OH are in the stoichiometric ratio, the rate equation in the mean-field limit[14] can be written as follows:

$$-\frac{\mathrm{d}[\mathrm{NCO}]}{\mathrm{d}t}=k[\mathrm{NCO}]^2[\mathrm{R}''_3\mathrm{N}]=k'[\mathrm{NCO}]^2 \qquad (1)$$

where we have included the catalyst concentration in the reaction rate constant. A simplified kinetic equation is thus obtained. The solution of equation (1) is an algebraic decay and given by:

$$[\mathrm{NCO}]=\left(k't+\frac{1}{[\mathrm{NCO}]_0}\right)^{-1} \qquad (2)$$

Or in terms of the extent of reaction p defined as $[\mathrm{NCO}]=[\mathrm{NCO}]_0(1-p)$, equation (2) becomes:

$$1/(1-p)=k'[\mathrm{NCO}]_0t+1 \qquad (3)$$

In our case, where the addition reaction was carried out in the presence of a catalyst, we can expect second-order kinetics until a conversion of 75%. The slope of the linear part of *Figure 6* yields a constant that represents a characteristic time τ for the gelation process. This time is related to the rate equation parameters by the relation:

$$\tau=\frac{1}{k[\mathrm{R}''_3\mathrm{N}][\mathrm{NCO}]_0}$$

where k, $[\mathrm{R}''_3\mathrm{N}]$ and $[\mathrm{NCO}]_0$ are the reaction rate constant, the catalyst concentration and the initial isocyanate concentration respectively. Experimentally the time τ is the slope of the linear part in the representation of $1/(1-p)$ *versus* time t in the pregel region. It is then possible to define a reduced time $t_r=t/\tau$, the ratio of the reaction time t to the characteristic time τ.

On *Figure 7* we have plotted the conversion p of the reaction *versus* this reduced time t_r for different samples. In *Table 1* are displayed some experimental values of the characteristic time τ. We can see that all the experimental points for p *versus* t_r lie on the same curve describing the quantitative effect of the addition reaction from the onset to an extent of reaction of 93%. This indicates that, in each case, the reaction proceeds in the same way as indicated on the reaction scheme shown above. In other words the same experimental behaviour can be reproduced in all experiments.

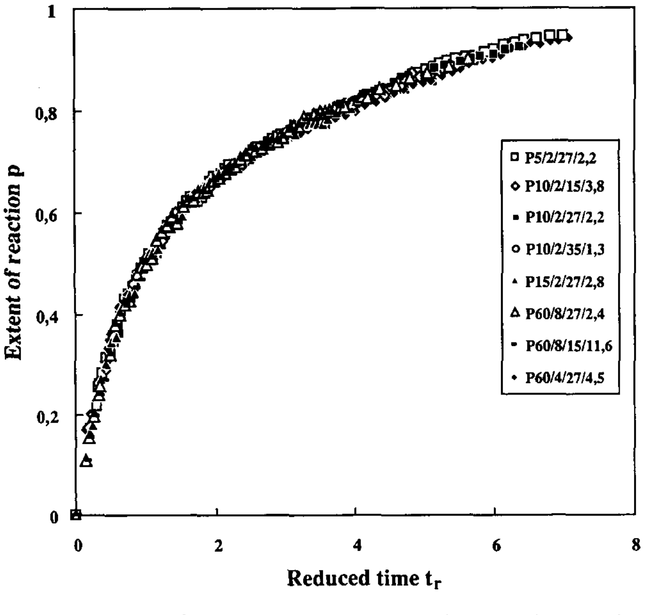


Figure 7 Extent of reaction p *versus* reduced time t_r. Whatever the system, all the experimental points lay on the same curve. All systems studied follow simple second-order kinetics below the gelation threshold

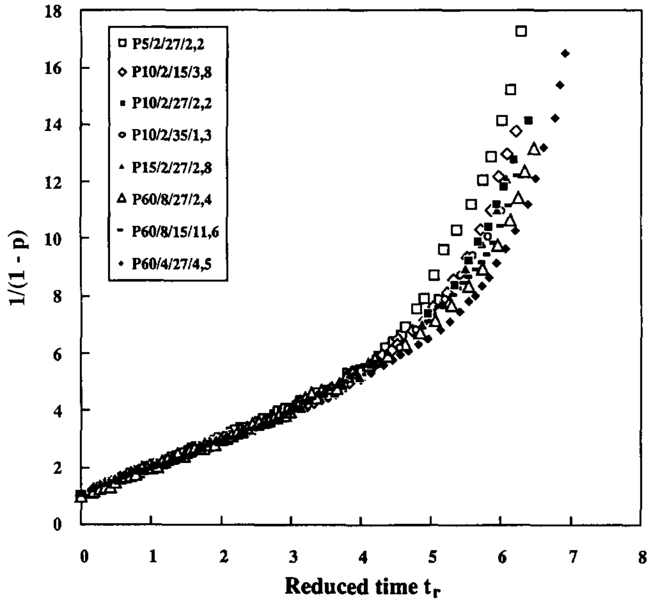


Figure 8 Variation of the ratio $1/(1-p)$ as a function of reduced time t_r

The same phenomenon is observed when $1/(1-p)$ is plotted *versus* time t_r (*Figure 8*), which indicates a simple second-order kinetics. Up to an extent of reaction of 75%, the experimental points given by the *FT*-i.r. measurements belong to a unique straight line as predicted by equation (1). From this extent of reaction onwards we observe a positive deviation due to the slowing down of the reaction rate.

Kinetics in the postgel region

The second-order reaction represented by equation (1) correctly describes the kinetics of the investigated systems at 25°C until a conversion of 75%, which corresponds approximately to the gel point. But above this conversion, the addition reaction follows a different kinetic behaviour. The kinetic curves deviate positively from the straight line observed in the pregel phase. The study of the kinetics of the reaction between a functional precursor polymer and a crosslinking agent leading to a three-dimensional system is much more complicated than in the case of the classical addition reaction involving hydroxyl and isocyanate functions belonging to small difunctional molecules. The principal difficulty encountered comes from the strong viscosity increase in the reaction medium due to the formation of very highly branched molecules[7,15]. The difficulty of such an investigation is enhanced even more when gel formation occurs. At conversions close to and below the gel point, the polymer species are very entangled and the local concentration of the functional groups is rather high. On the other hand the mobility of the reagents is reduced. The diffusion process becomes a very important parameter, which controls the kinetics of the reaction. The reduced mobility of the neighbouring functional groups could favour intramolecular reactions in this system. These factors could be responsible for the sudden increase in the overall reaction velocity above 75% conversion.

Changes in the apparent reaction rate for the reaction of isocyanates with alcohols were frequently observed by several authors. Meyer *et al.*[16] have observed an increase in the reaction velocity but they did not give any explanation for this phenomenon. The system polyoxypropylenetriol/toluene diisocyanate studied by Vilesova *et al.*[17] was described by an overall second-order reaction rate. In this case the kinetics was not affected by the gelation process and did not depend on the extent of reaction. Anzuino *et al.*[18] explained a slight velocity increase for the reaction of α,ω-dihydroxypoly(oxytetramethylene) by allophanate formation. However, for most systems the above side-reaction becomes significant only at elevated temperatures (above 100°C). Notice that the NH group concentration is not affected by the allophanate formation. A theoretical approach describing the pregel and the postgel kinetics is the spanning-tree approximation for f-functional polycondensation processes incorporating cyclization reactions. This was achieved successfully by Gordon *et al.*[19–21]. The mathematical calculation of the rate equations is very complex and therefore not attempted in this work; but their model takes into consideration first-shell substitution effects as well as the competition between intra- and intermolecular reactions. Dusek *et al.*[22] have developed a theoretical approach based on the theory of branching processes to describe gelation and network formation of polyurethanes due to side-reactions of the α,ω-dihydroxypoly(oxypropylene) and bis(4-isocyanato)phenylmethane system catalysed with dibutyltin dilaurate at 60–140°C. They did not report a kinetics study concerning this system.

CONCLUSION

The results obtained in our investigation are in an excellent agreement with those reported earlier by Feger and coworkers[23] on a comparable system. Though a reaction that involves a gelling process is rather complex, the kinetics of the crosslinking reaction can be followed in a quite broad range by *FT*-i.r. spectrometry, provided that at least one of the reacting species has a characteristic strong absorption band. The extent of the reaction can be easily monitored by this technique. Using this method, we have established that the reaction between the hydroxyl groups of the functional prepolymers and the isocyanate functions of the crosslinking agent follows second-order kinetics in the conversion range below approximately 75% (pregel region). Within this range of the extent of reaction all the systems we have investigated present the same behaviour. For conversions above the gel point ($\approx$83%) we note a positive deviation from the second-order kinetics, i.e. an acceleration of the reaction rate. If we consider the theoretical approach of Gordon *et al.*, this behaviour could be explained by an increasing contribution of intramolecular reactions. However, this statement needs more experimental support and further experimental data are required.

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