Rheokinetic study of crosslinking of α,ω-dihydroxy oligo(alkylene maleate)s with a trisisocyanate

BRANKO DUNJIĆ[1*#], JASNA DJONLAGIĆ[1#], SLAVKO VUKAŠINOVIĆ[1], MAURICE SEPULCHRE[2], MARIE-ODILE SEPULCHRE[2] and NICOLAS SPASSKY[2]

[1]*Faculty of Technology and Metallurgy, Karnegijeva 4, YU-11000 Belgrade, Serbia and Montenegro and* [2]*Laboratoire de Chimie Macromoléculaire, Université Pierre et Marie Curie, 4, Place Jussieu, 75005 Paris, France*

Abstract: The crosslinking reaction of three series of α,ω-dihydroxy oligo(alkylene maleate)s with a trifunctional isocyanate was followed by dynamic mechanical analysis and FTIR spectroscopy. The evaluation of rheological parameters, such as storage G' and loss modulus G'', was recorded. A typical G' *versus* time curve has a characteristic "S" shape, indicating autoacceleration of the crosslinking reaction. The whole curing process starting from G' equal G'' or the beginning of gelation is described by a second-order phenomenological rheokinetic equation which takes into account the autoacceleration effect, the latter being a consequence of the superposition of both the chemical reaction and phase segregation. It appears that the crosslinking reaction rate depends on the concentration of the functional groups, *i.e.*, on the molecular weight of the polyester prepolymer and on the length of the aliphatic sequence in the repeating unit or the segmental mobility. The crosslinking rate decreases in the order: poly(octamethylene maleate) > poly(hexamethylene maleate) > poly(butylene maleate).

Keywords: hydroxyl terminated polymaleates, polyurethane, rheokinetic analysis.

INTRODUCTION

Polymer networks as well as model polymer networks, with well defined structural characteristics, have been the subject of many theoretical and experimental investigations.[1,2] In this paper, polyurethane model networks containing elastic polyester chains were synthesized by the stoichiometric end-linking reaction between a hydroxy terminated prepolymer and a trifunctional isocyanate crosslinker. The prepolymers were bifunctional hydroxy terminated polyesters of known molecular weight, *i.e.*, α,ω-dihydroxy oligo(alkylene maleate)s, while triisocyanate was the crosslinking agent. The polyurethane networks were produced by polyaddition crosslinking reactions, while control of the length and of the number of elastic chains was ensured. Fourier transform infrared spectroscopy (FTIR) was used to describe the

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*   Corresponding author.

\#   Serbian Chemical Society active member.

chemical kinetics of network formation, *i.e.*, to establish the order of the reaction before the gel point and the extent of reaction at the gel point. In order to monitor the evoluation of the dynamic rheological parameters, dynamic mechanical spectroscopy was used. However, only a few polyurethane systems have been investigated during the whole process of network formation, *i.e.*, from the initial state until fully cured network.[3]

The present rheological study of the crosslinking reaction of α,ω-dihydroxy oligo(alkylene maleate)s with trisisocyanate is a continuation of previous studies on the relationship between the structure and the properties of configurationally pure unsaturated polyesters.[4–6] Hydroxyl terminated stereoregular polymaleates could be used as prepolymers in synthesis of model polyurethane networks due to the high flexibility of their polymer chains and telechelic structure.[7]

The experiments performed by Winter and Chambon[8] involved polymer networks which could be modeled as an ideal system. For an ideal system, crosslinking occurs at the ends of the polymer molecules. The initial molecular weight of the prepolymer is such that entanglements are excluded, no intramolecular crosslinking occurs, only intermolecular crosslinking and the formed crosslinks are permanent. Rampp *et al.*[9] anticipated that a network produced by the end-linking method could contain a few unavoidable defects, like: dangling chains, arising from either incomplete conversion or a local excess of one kind of function, or loops. The gel point method developed by Winter and Chambon[8] utilized the loss tangent, *tan*(δ), obained from dynamic oscillatory measurements. At the gel point, *i.e.*, the instant when a solution transforms from viscous liquid behaviour to a solid that contains an extended network, the storage and loss modulus should display the same frequency dependence. On further crosslinking, the elastic modulus of the sample becomes greater than the viscous modulus throughout the frequency range and also independent of frequency, which are characteristics of a highly crosslinked gel.

A basic variable in the case of rheological investigations of the curing of polymers is the dynamic storage modulus, *G'*, which is proportional to the crosslink density of the network being formed by chemical bonds and physical entanglements. Its change with time very often exhibits an autocatalytic "S"-shape. This effect can be influenced by many different phenomena, such as chemical self-catalysis, the gel-effect, the appearance of local heterogeneities and the parallel course of different reactions. The most important factor determining the time dependence of the rheological conversion described is phase separation. Thus, the superposition of the effects of both chemical crosslinking and morphology change results in the self-acceleration shape of the rheological conversion *vs.* time dependence.

It has been proposed by Malin and Kulichikhin[10,11] that the rheokinetics of the curing of a heterogeneous reactive system can be described by the following phenomenological equation containing a self-acceleration term:

$$\mathrm{d}\beta/\mathrm{d}t = k(1 + c\beta)(1 - \beta)^n \tag{1}$$

where β is the rheological degree of conversion, t is time, k and c are temperature dependent constants and n is the reaction order.

In this paper we wish to report on a kinetic study of the crosslinking of three series of α,ω-dihydroxy oligo(alkylene maleate)s with a trisisocyanate. The crosslinking was followed by both dynamic mechanical and FTIR spectroscopy. A rheokinetic model of crosslinking and network formation is proposed to confirm the autocatalytic character of these reactions and to determine the numerical values of the constants of the rheokinetic equation and the degree of rheological conversion as a function of time. The effects of both the molecular weight of the prepolymer and the length of the aliphatic sequence in the repeat unit on the curing kinetics of these model polyurethane networks were examined.

EXPERIMENTAL

Materials

The polymer precursors used in this study were three series of α,ω-dihydroxy oligo(alkylene maleate)s. The synthesis and characterization of these unsaturated polyesters were described in detail in a previous paper.[7] Their principal characteristics are presented in Table I.

TABLE I. Characterization of the α,ω-dihydroxyoligo(alkylene maleate)s, number average molecular weight

Sample	$\overline{M}_n$	$\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{f}^{a)}$	$\overline{f}^{b)}$
	(VPO)	(NMR)	(GPC)			
PBM(OH)1	1800	1900	1750	1.25	1.90	1.85
PBM(OH)2	2200	2400	1900	1.35	1.85	1.60
PBM(OH)3	2500	3100	2600	1.40	1.60	1.70
PHM(OH)1	2000	1900	1700	1.30	2.10	1.80
PHM(OH)2	2400	3600	2700	1.50	1.35	1.50
PHM(OH)3	–	4900	3800	1.30	–	1.55
POM(OH)1	1100	1900	1900	1.30	1.20	2.00
POM(OH)2	1400	2150	2300	1.35	1.30	2.10
POM(OH)3	1700	3550	3300	1.45	1.0	1.90

[a)]Mean functionality: $\overline{f} = 2\,\overline{M}_{VPO}/\overline{M}_{NMR}$; [b)] Mean functionality: $\overline{f} = 2\,\overline{M}_{GPC}/\overline{M}_{NMR}$

The crosslinking agent, tris-(4-isocyanatophenyl) thiophosphate (Desmodur DRF, Bayer, in the form of a 30 % solution in ethyl acetate) was recrystallyzed from ethyl acetate. The content of NCO was determined according to ASTM. The NCO content was found to be 26.1 wt. % which represents a purity of 96.5 %.

Sample preparation

All the samples for crosslinking were prepared in the same way: the ratio NCO/OH was 1.00. A weighed amount of triisocyanate was dissolved in 0.35 ml of CH_2Cl_2. The solution was then added to a weighed amount of the polyester and mixed well. After mixing the reagents, the solvent was evaporated under reduced pressure (1 mm Hg). The prepared sample was simultaneously transferred to a Dynamic Mechanical Spectrometer and to an FTIR spectrometer. All the operations were performed within 12 min.

Rheological measurements

The storage (G') and loss (G'') shear moduli of the reaction mixture were recorded using a Rheometrics Mechanical Spectrometer RMS-605 operating in the dynamic shear mode between two parallel plates at a

constant frequency of 6.28 rad/s (1 Hz) at a temperature of 30 ± 1 ºC. The diameter of the plates was 25 mm and the gap between the plates was 1 mm. Repeated dynamic measurements were taken at programmed 0.5 min intervals to monitor the build-up of the network structure.

FTIR measurements

FTIR spectra were taken of films of the unsaturated polyester/triisocyanate reaction mixture cast on NaCl plates at programmed time intervals which changed depending on the rate of crosslinking. Transmission spectra were obtained using a Nicolet spectrometer.

The peak area of the NCO group (ν, cm^{-1}, 2273) was normalized to the peak of the methyl group whose intensity was unaffected by crosslinking. The extent of the reaction was then calculated as

$$p = \frac{A_0 - A}{A_0}$$

where A_0 is the normalized absorption of the NCO peak of the unreacted reaction mixture and A is normalized absorption of the NCO peak corresponding to a reaction time t.

Due to the high reaction rate and to the fact that 12 min were required for the preparation of the sample, the initial peak area was determined by using a calibration curve. The calibration curve was constructed by taking spectra of a series of mixtures of isocyanate with corresponding unsaturated polyesters which did not have OH terminal groups.

Mathematical data analysis

The computer program Table Curve TM 2D was used to fit the experimental data, *i.e.*, $d\beta/dt - \beta$ by a selected form of the kinetic expression. After confirmation that the exprimental and calculated values fitted well, the kinetic parameters were determined.

RESULTS AND DISCUSSION

Structure and molecular weight of the hydroxy-terminated polymaleates

α,ω-Dihydroxy oligo(alkylene maleate)s with molecular weights ranging from 1500 to 4000 g/mol were synthesized by the low-temperature heterogeneous polycondensation of potassium maleate and either 1,4-dibromobutane, 1,6-dibromohexane or 1,8-dibromooctane in the presence of 2-bromoethanol. The monofunctional reactant, 2-bromoethanol, was used as a regulator of the molecular weight and for the introduction of hydroxyl groups at both chain ends. The general structure of the three series of hydroxyl-terminated oligomaleates is given below:
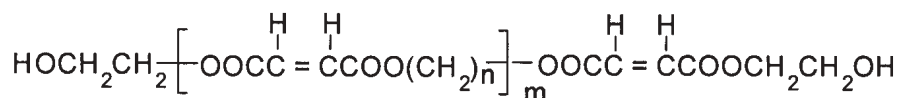
n = 4, 6 and 8
n = 4, PBM(OH); n = 6, PHM(OH); n = 8, POM(OH)

The synthesis and structure of the telechelics examined in this study have been previously described in detail.[7] The characteristics of the hydroxyl-terminated stereoregular unsaturated oligo(alkyl maleate)s are given in Table I. It can be seen that the calculated values of $\overline{M}_n$ (on the basis of the amount of 2-bromoethanol) are close to the experimentally found
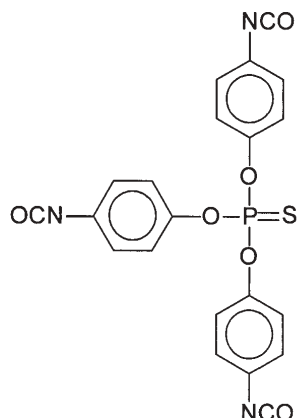
Fig. 1. Tris (4-isocyanatophenyl) thiophosphate (Desmodur DRF).

values. The mean functionality of the polyester samples was reasonably close to 2. Most of the values, slightly higher or lower than two, are in the range of experimental error, which are the consequence of the inaccuracy of the molecular weight determinations. Hydroxyl-terminated polymaleates with $\bar{f} \approx 2$ and narrow molecular weight distributions were used as prepolymers for the formation model of the polyurethane networks.

The crosslinking was achieved by reacting the polyesters with tris(4–isocyanatophenyl)thiophosphate (Fig. 1) which results in trifunctional junctions as the crosslinking points. In order to obtain a homogeneous mixture, the trisisocyanate was dissolved in dichloromethane and then added to the polyester. After mixing, the solvent was removed by evaporation under reduced pressure at room temperature. All these operations were completed in about 12 min. Usually, homogeneous mixtures of this trisisocyanate are made by heating the suspension of trisisocyanate at 90 ºC.[12] This was not possible in our case due to the high reactivity of the terminal hydroxyl groups. After evaporation of the solvent, the mixture was transferred simultaneously to a Dynamic Mechanical Spectrometer and to an FTIR spectrometer, in order to follow the crosslinking by both the rheological and IR spectroscopical methods.

Crosslinking behavior from the rheological study

A typical change of the storage modulus (G') and loss modulus (G'') with time for the reaction mixture PBM(OH)1 is shown in Fig. 2. All measurements were repeated in order to check the reproducibility. It was established that the accordance between the measurements was ± 5 %. The change in rheological properties of a curing reaction mixture is directly proportional to the extent of the reaction. For example, the gel time could be determined according to different criteria.[13–15] One criterion is the peak maximum in the tangent angle of mechanical loss ($tan\,\delta$)$_{max}$ where the difference between the elastic and the viscous behavior of the reaction mixture is maximal. Another criterion is the crossover of $G'\,vs.\,t$ and $G''\,vs.\,t$ curves, at which point the system shows the same level of elastic and viscous behavior, which means that the same quantity of energy is stored and dissipated. Or it could be determined as the intersection point of the tangent on the curve G' (100 kPa) and the base line ($G'' = 0$).
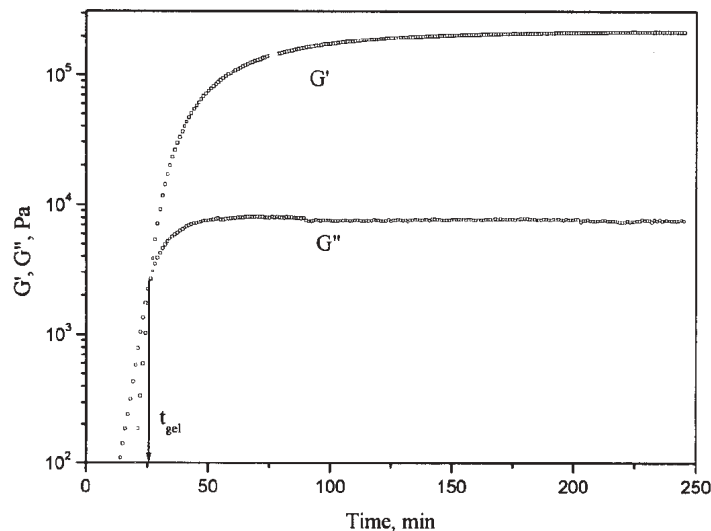
Fig. 2. Evolution of the storage *G'* and loss *G''* moduli as functions of reaction time at 30 ºC and frequency 6.28 rad/s for reaction mixture PBM(OH)1.

We accepted the criterion corresponding to the crossover between the *G'* and *G''* curves, the point at which the system exhibits not only elastic but also viscous behavior, *i.e.*, the amount of energy stored is similar to the amount of the energy dissipated. This criterion is not a general criterion for determining the gel point. The gel point coincides with the crossover only when the storage and loss moduli are proportional to $\omega^{1/2}$ for stiochiometrically balanced network polymers and networks with excess crosslinker, as was reported by Winter *et al.*[16,17] The gel time values obtained for the curing of the α,ω-dihydroxy-terminated polymaleates with trisisocyanate crosslinker under isothermal condition depended on the molecular weight of the prepolymer, as well as on the chain flexibility (Table II).

TABLE II. Some characteristic parameters of curing the unsaturated polyesters with trisisocyanate, τ-is the characteristic time determined from FTIR measurements, *i.e.* the time before the gel point, gel point and inflection point

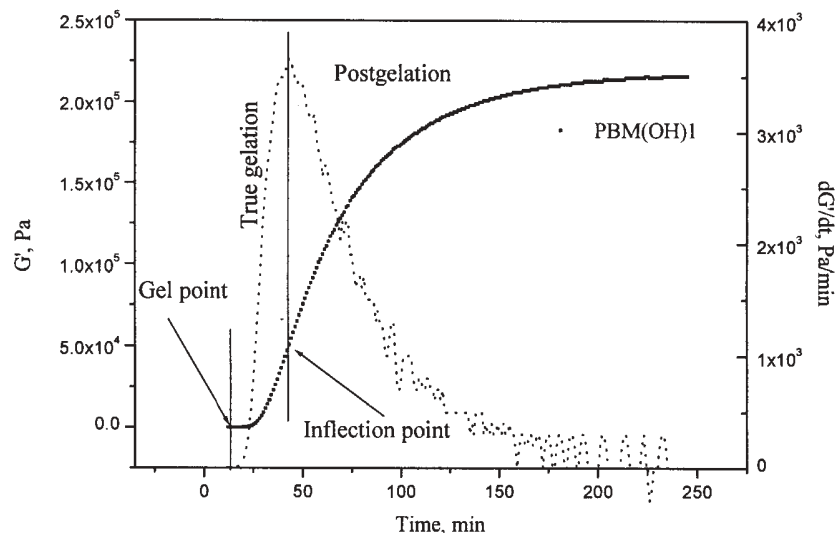| Sample	τ (FTIR)		Gel point		Inflection point characteristics		
	τ/min	p(IR)	$t_{G'=G''}$/min	p(IR)	t/min	β	p (IR)
PBM(OH)1	20	0.78	27	0.84	50	0.238	0.94
PBM(OH)2	26	0.75	52	0.87	88	0.251	0.92
PBM(OH)3	55	0.75	67	0.77	97	0.355	0.81
PHM(OH)1	14	0.78	18	0.87	25	0.230	0.95
PHM(OH)2	17	0.86	25	0.94	42	0.514	0.99
PHM(OH)3	23	0.83	152	–	192	0.504	–

Fig. 3. Storage modulus G', and the rate of its change, dG'/dt, for the reaction of the mixture PBM(OH)1, plotted linearly as a function of reaction time at 30 ºC. The stages of the crosslinking reaction are marked.

TABLE II. Continued

Sample	τ (FTIR)		Gel point		Inflection point characteristics		
	τ/min	p(IR)	$t_{G'=G''}$/min	p(IR)	t/min	β	p (IR)
POM(OH)1	13	0.83	15	0.89	20	0.365	0.95
POM(OH)2	11.5	0.76	15	0.85	20	0.242	0.94
POM(OH)3	12	0.74	19	0.91	25	0.233	0.95

A typical G' *vs.* t curve (Fig. 3) has a characteristic "S"-shape, indicating an autoacceleration of the crosslinking reaction. The rate of increase of the storage modulus with reaction time, dG'/dt, increases until the inflection point but subsequently decreases.

In our previous paper,[4] it was proposed that the crosslinking could be divided into three stages. These stages are represented in Fig. 3. In the pregelation stage, the molecular weight and branching of the oligomers increase as a result of the coupling reactions. True gelation is the stage between the point at which G' equals G'' and the point at which dG'/dt reaches its maximum (*i.e.*, inflection point). During this stage gel and sol co-exist in the reaction mixture and further coupling reactions not only enhance the crosslink density of the gel, but also progressively transform the sol fraction into the gel. Postgelation crosslinking follows after the inflection point.

Kinetics in the pre-gel region

The addition reaction of hydroxyl-terminated polyesters and Desmodur DRF was carried out at 30 ºC. In the absence of side reaction, the variation of the NCO concentration
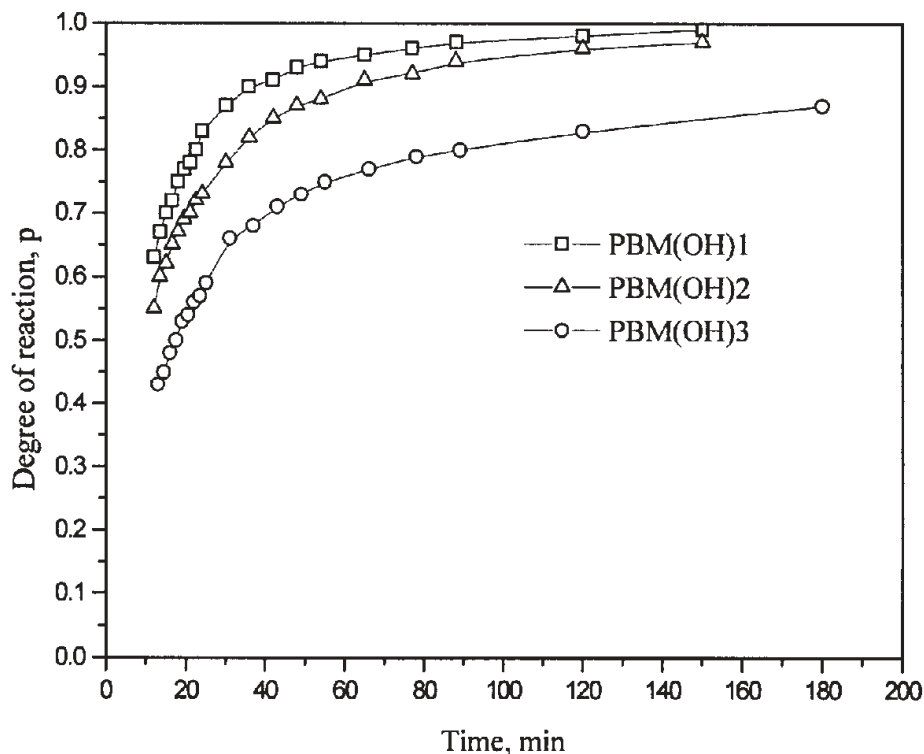
Fig. 4. Degree of reaction *p versus* time for the crosslinking reaction of the PBM(OH) series of
hydroxyl-terminated polymaleates with the triisocyanate at 30 ºC.

can be considered to be due only to the reaction between hydoxyl and isocyanate groups.
The results obtained from the FTIR-measurements are presented in Fig. 4, where the degree of reaction is plotted as a function of time *t* of the curing reaction for the PBM(OH) series. The concentration of the two functional groups was stoichiometric and assuming that the reaction is second order, the rate equation can be written as follows:

$$-\frac{d[NCO]}{dt} = k'[NCO]^2 \qquad (2)$$

In terms of the extent of the reaction *p*, the integral form of Eq. (2) becomes:

$$\frac{1}{(1-p)} = k'[NCO]_0 \; t + 1 \qquad (3)$$

A plot of $1/(1-p)$ *versus* time *t* obtained from FTIR-measurements is shown in Fig. 5, from which it can be seen that the formation of the urethane function follows simple second-order kinetics until an extent of reaction of 75 %, which corresponds approximately to the gel point. For conversions above the gel point, a positive deviation from the second order kinetics, *i.e.*, an increase in the overall reaction rate, was observed. Hakiki *et al.*[18] ob-
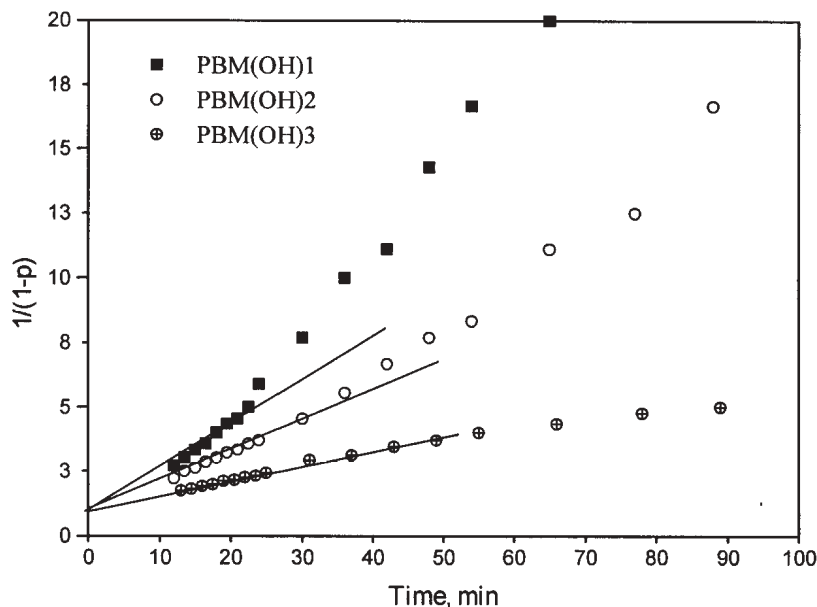
Fig. 5. Variation of the ratio $1/(1-p)$ as a function of time for the crosslinking reaction of the PBM(OH) series with triisocyanate at 30 °C.

served similar behavior during the crosslinking of HO-functional polystyrenes with a trifunctional crosslinker which they attributed to an increase in the contribution of intramolecular reactions.

The characteristic parameters of the curing of the three series of unsaturated α,ω-dihydroxy poly(aklyl maleate)s, such as the time τ-time until the gel point, determined as the commencement of the deviation from linearity of the function $1/(1-p)$ *versus* time and the corresponding degree of reaction from FTIR measurements; the time of the gel point from rheological measurements, determined as $G' = G''$, the time of the attainment of the inflection point, the rheological conversion and its rate at the inflection conversion, are presented in Table II. It may be noted that τ as well as the gel time and the time and conversion at the inflecton point are dependent on both the functional NCO (or OH) group concentration (*i.e.*, the molecular weight of the polyester glycol) and the number of carbon atoms in the repeating units of the polyesters chains.

Study of post-gelation region

In order to understand the physical meaning of the inflection point on the G' *vs. t* curves (*i.e.*, the maximum of the rheological rate of crosslinking), the reaction of network formation was followed by FTIR spectroscopy. The degree of reaction (p) and rheological conversion (β) of polyurethane network formation are shown in Fig. 6. The chemical conversion increased very rapidly during the initial stage of the curing reaction, while an appreciable rheological conversion could be detected near the gel point.

The results confirmed that the uncatalysed reaction between NCO and OH was un-
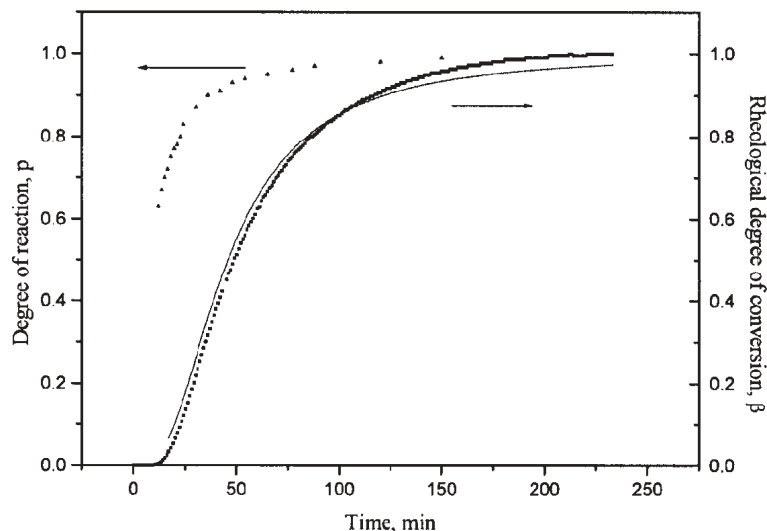
Fig. 6. Degree of reaction *p* and degree of rheological conversion *β* (experimental - symbols and calculated - line) plotted as a function of the curing time of PBM(OH)1. The chemical conversion increased very rapidly during the initial stage of the curing reaction, while an appreciable rheological conversion could be detected near the gel point.

usually rapid at room temperature,[7] hence, due to the high reaction rate, it was only possible to follow the reaction from 40 % (in the case of poly(butylene maleate)) and from 55 % (in the case of poly(octamethylene maleate)) conversion. In general, the extent of the reaction was greater than 50 % after the 12 min necessary for the operations of mixing and evaporation of the solvent.

The degree of reaction *p* at the inflection point on *G' vs. t* curves (*i.e.*, at the beginning of gel crosslinking) decreases as the rate of cure increases. Thus, p_{FTIR} at the inflection point varies from 0.81 to 0.93, in the case of PBM(OH)s, from 0.95 to 0.99 in the case of PHM(OH)s and it is around 0.95 for POM(OH)s.

TABLE III. The results of the rheokinetic measurements for postgelation crosslinking

Sample	$\overline{M}_n$ (GPC) g/mol	Duration of the true gelation stage/min		$G'=G''$/kPa	$G'_{infl.}$/kPa	G'_{∞}/kPa	$G'_{infl.}/G'_{\infty}$
		Start	End				
PMB(OH)1	1750	27	50	1.05	41.43	174	0.238
PBM(OH)2	1900	52	78	2.74	22.78	90.6	0.251
PBM(OH)3	2600	67	97	2.56	3.63	10.2	0.355
PHM(OH)1	1700	18	25	4.80	65.33	81.5	0.230
PHM(OH)2	2700	13	42	4.30	12.18	23.3	0.514
PHM(OH)3	3800	140	46	5.30	9.03	19.7	0.504
POM(OH)1	1700	15	33	4.40	16.12	44.0	0.365

Sample	$\overline{M}_n$ (GPC) g/mol	Duration of the true gelation stage/min		$G'=G''$/kPa	$G'_{infl.}$/kPa	G'_∞/kPa	$G'_{infl.}/G'_\infty$
		Start	End				
POM(OH)2	2300	15	34	2.80	24.97	102.3	0.242
POM(OH)3	3300	19	38	3.00	16.04	70.4	0.223

In a previous paper,[4] the inflection point was associated with the moment when the sol fraction (w_s) falls below a certain value, so from that moment the increase of G' is the consequence of increasing crosslink density only, and not of the transformation of liquid sol into solid gel. The obtained results in almost all cases confirmed that the sol fraction calculated from Flory's gelation theory in the inflection point was always below 1 wt. %. As to the importance of post-gelation curing, over 70 % of the G' of a maximally crosslinked polyester had to be gained during the post-gelation period (Table III). It is also evident that the duration of the post-gelation curing is several times longer than the duration of gelation.

Rheokinetic model of curing polymaleates

From both a theoretical and a practical point of view, rheokinetic models enable the entire process of network formation to be followed and the mechanical properties of the final material to be predicted. The rheokinetic model proposed by Malkin and Kulichikchin for thermoreactive polymer curing was used for analyzing the network formation of polyurethanes. In this model the process of crosslinking is described by the equation which includes a self-acceleration term:

$$\frac{d\beta}{dt} = k\beta^m (1-\beta)^n \tag{4}$$

where k is the temperature dependent rate constant and m and n are empirically selected constants, the sum of which represents the reaction order. Actually, in this work Eq. (4) was used in the form with $m+n=2$, and β is the rheological extent of reaction, which is a function of the storage modulus $G'(t)$ defined as:

$$\beta = \frac{(G'_t + G'_0)}{(G'_\infty - G'_0)} \tag{5}$$

where G'_0 represents the value of the storage modulus at zero time, or at the beginning of the crosslinking, and G'_∞ is the value of the storage modulus of the maximally crosslinked polymer.

The differential Eq. (4) has the analytical solution:

$$\beta = \frac{\sqrt[1-m]{k(1-m)t}}{1 + \sqrt[1-m]{k(1-m)t}} \tag{6}$$

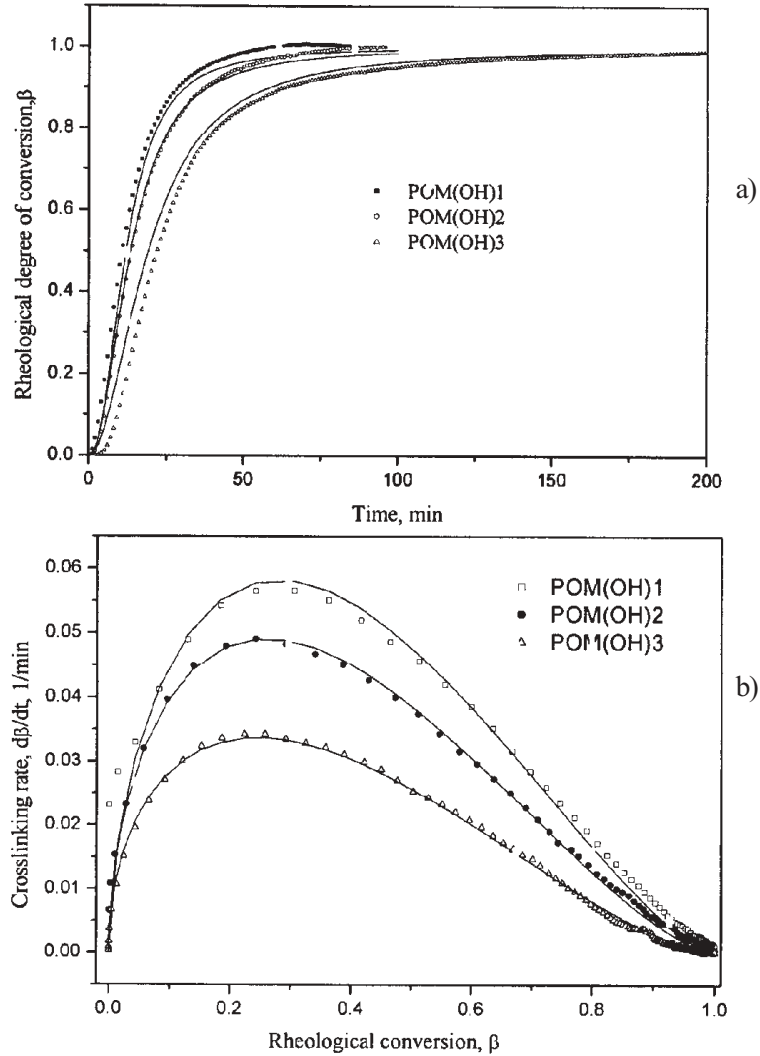Hence the experimental and calculated dependencies of the rheological degree of

Fig. 7. a) Degree of rheological conversion β *versus* time at 30 °C for POM(OH) series. Symbols: experimental values of β; lines: calculated values. b) Experimental data fitted with the expression $\dfrac{\mathrm{d}\beta}{\mathrm{d}t} = k\beta^{m}(1-\beta)^{2-m}$ for POM(OH) series. Symbols: experimental values of β; lines: calculated values.

conversion β on time can be compared graphically. It can be seen in Fig. 7(a) and (b) that good agreements between the experimental and calculated dependencies of the degree of conversion on time and on rate of conversion over the entire conversion were obtained. This confirmed that the proposed rheological model is good and that self-acceleration, as a consequence of the chemical reaction of crosslinking and morphological changes, occurs. The self-acceleration model can be used when the maximum reaction rate is observed at around 30 % of the rheological conversion, as is the case in the curing reaction of telechelic
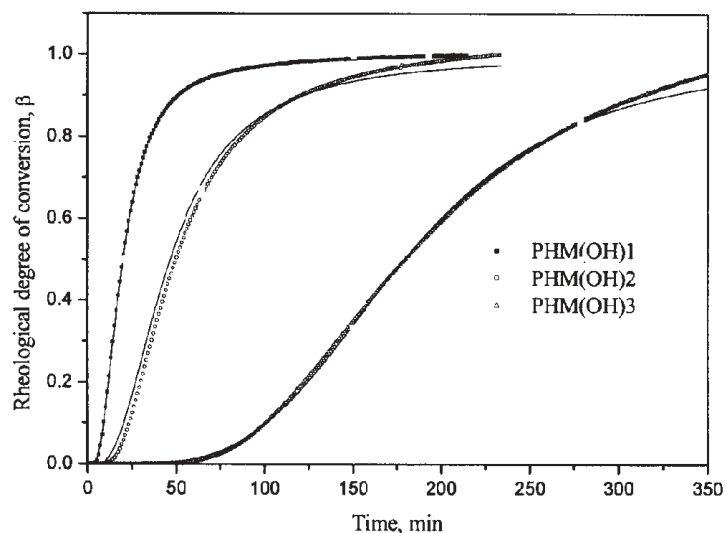
Fig. 8. The influence of the molecular weight on the crosslinking rate for the PHM series.

polymaleates and a triisocyanate.The curves were fitted with the above equation and the values of the obtained kinetic parameters k, m and n are given in Table IV. The viability of fitting the experimental data, *i.e.*, $d\beta/dt$ *vs.* β, by the selected form of kinetic expression is confirmed by the values of the correlaton coefficient r^2, given in Table IV.

TABLE IV. Kinetic parameters of crosslinking hydroxyl-terminated polymaleates with triisocyanate given by fitting of experimental data with the expression $d\beta/dt = k\,\beta^m(1-\beta)^{2-m}$

Sample	$\overline{M}_{nGPC}$	Inflection point		$k \times 10^2/min^{-1}$	m	$n = 2-m$	r^2
		β	$\times 10^3\ d\beta/dt$				
PBM(OH)1	1750	0.262	16.5	5.17	0.514	1.486	0.988
PBM(OH)2	1900	0.299	10.2	3.44	0.594	1.406	0.989
PBM(OH)3	2600	0.384	9.2	3.39	0.749	1.251	0.788
PHM(OH)1	1700	0.256	39.8	12.51	0.522	1.478	0.999
PHM(OH)2	2700	0.268	16.4	5.21	0.526	1.474	0.993
PHM(OH)3	3800	0.355	5.6	2.09	0.713	1.287	0.931
POM(OH)1	1900	0.28	58.2	19.12	0.562	1.438	0.959
POM(OH)2	2300	0.25	49.0	15.48	0.521	1.479	0.993
POM(OH)3	3300	0.256	34.2	10.31	0.492	1.508	0.998

The influence of the molecular weight of the prepolymer is illustrated in Fig. 8, where the crosslinking of the three samples of poly(hexamethylene maleate)s are shown. A comparison of polyesters with the same molecular weight but synthesized with different dibromoalkanes is shown in Fig. 9. The rate of crosslinking as a function of molecular weight of the prepolymer is shown in Fig. 10 for all three series. From Fig. 10 it can be seen
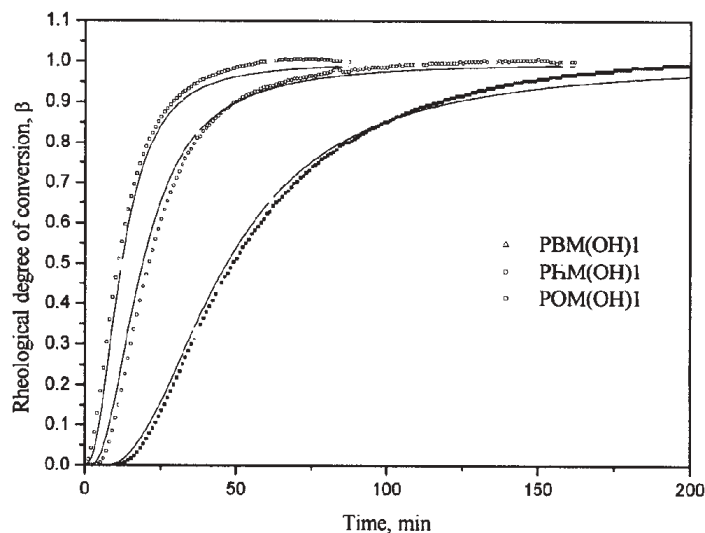
Fig. 9. The influence of the chain flexibility of the prepolymer on the rate of crosslinking.
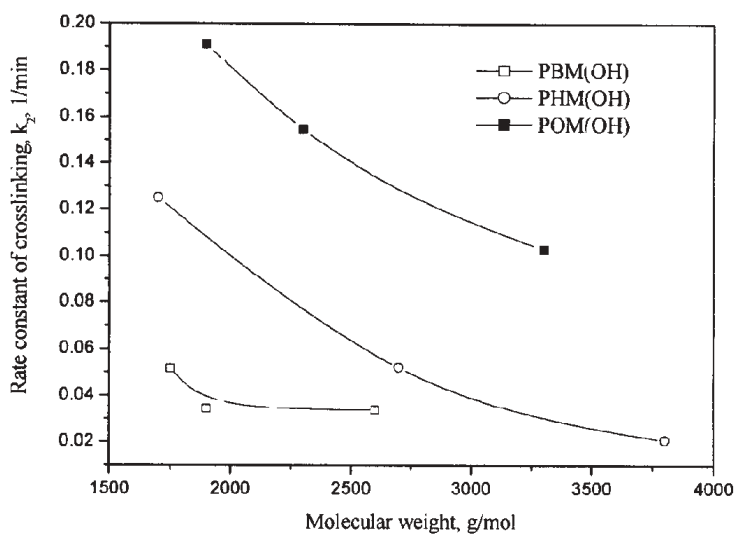

Fig. 10. Influence of the molecular weight of the polyester prepolymer on the crosslinking rate.

that the rate of crosslinking decreases in the order poly(octamethylene maleate) > poly(he-xamethylene maleate) > poly(butylene maleate). As the NCO concentration is approximately the same for all the samples, the difference in the crosslinking rate can only be due to the difference in chemical composition. It could be concluded that poly(octamethylene maleate) has the greatest chain mobility and that this influences the rate of crosslinking. This implies that the apparent reactivity of a functional group is dependent on the size and mobility of the precursor.

The dependence of k on the number of carbon atoms in the dibromoalkane used for
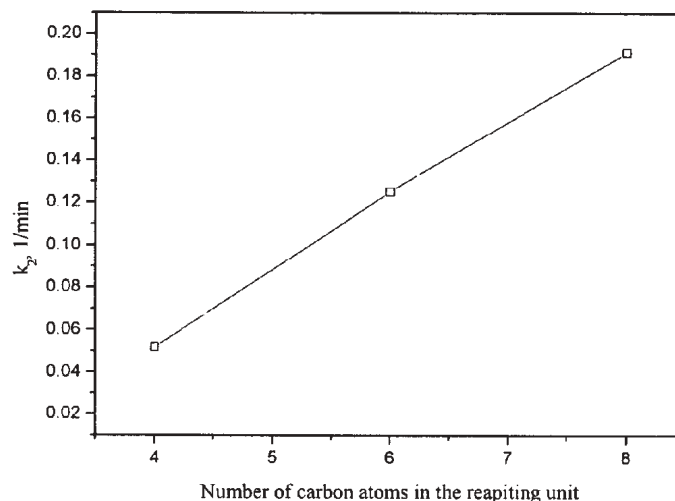
Fig. 11. The reaction rate of crosslinking depends on the length of the aliphatic sequence in the repeating unit *i.e.*, on the chain flexibility and segment mobility.

the synthesis is plotted in Fig. 11. For the series of poly(butylene maleate)s, the values of the rate constant k_2 are in the range from 0.03 to 0.05. The rate constants for the poly(octamethylene maleate) series are 4 times greater. The values for the PHM(OH) series lie between the two extreme cases. Once again it is obvious that the crosslinking rate is strongly dependent on chemical composition, *i.e.*, segmental mobility. This approach allows the prediction of G' during the whole process.

CONCLUSION

The crosslinking reaction of three series of hydroxyl terminated stereoregular unsaturated polyesters was followed by both FTIR spectroscopy and dynamic mechanical spectroscopy. The combination of these two methods is a powerful tool in monitoring changes in the chemical and rheological conversion during polyurethane network formation. The crosslinking reaction was very rapid even at room temperature and follows second order kinetics until an extent of reaction of 75 %, which corresponds approximatelly to the gel point. Above the gel point, a positive deviation from second order kinetics as a consequence of an acceleration of the reaction rate was observed. The obtained rheological data permit the whole process of crosslinking to be described. The equation $d\beta/dt = k\beta^m(1 - \beta)^{2-m}$, which includes a self-accelereation term, describes the whole process well. The rate constant, k, is dependent on the segmental mobility. Thus, the crosslinking rate decreases in order poly(octamethylene maleate) > poly(hexamethylene maleate) > poly(butylene maleate). The chemical extent of reaction was determined by FTIR analysis, which permitted the sol content at the beginning of postgelation curing, *i.e.*, the inflection point, to be calculated. This confirmed that the sol content at gelation was less than 1 wt.%, and that in postgelation crosslinking all the functional groups are attached to the network, and that the reaction rate depends exclusively on the segmental mobility.

И З В О Д

РЕОКИНЕТИЧКО ИЗУЧАВАЊЕ УМРЕЖАВАЊА α,ω-ДИХИДРОКСИ
ОЛИГО(АЛКИЛЕН МАЛЕАТА) ТРИИЗОЦИЈАНАТИМА

БРАНКО ДУЊИЋ[1], ЈАСНА ЂОНЛАГИЋ[1], СЛАВКО ВУКАШИНОВИЋ[1], MAURICE SEPULCHRE[2],
MARIE-ODILE SEPULCHRE[2] и NICOLAS SPASSKY[2]

[1]*Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, 11000 Београд,* [2]*Laboratoire de Chimie
Macromoléculaire, Université Pierre et Marie Curie, 4, Place Jussieu, 75005 Paris*

Кинетика реакције умрежавања је изучавана помоћу динамичке механичке анализе и
FTIR спектроскопије на три серије α,ω-дихидрокси-олиго(алкилен-малеата) и трифункцио-
налног изоцијаната. Реакција умрежавања полимера праћена је преко промене реолошких
параметара као што су модул сачуване енергије G' и модул изгубљене енергије G''. Крива
зависности G' од времена има карактеристичан "S" облик, што указује на самоубрзавање при
реакцији умрежавања. Цео процес умрежавања од почетка желирања, односно, од тренутка
када је G' једнако G'', је описан феноменолошком реокинетичком једначином другог реда која
узима у обзир ефекат самоубрзавања, као последицу суперпозиције хемијске реакције и
морфолошких промена. Показано је да брзина реакције умрежавања зависи како од концен-
трације функционалних група, тј. од моларне масе полиестарског претполимера, тако и од
дужине алифатичне секвенце у основном мотиву или сегменталне покретљивости. Брзина
реакције умрежавања опада у низу: поли(октаметилен–малеат) > поли(хексаметилен–малеат)
> поли(бутилен–малеат).

(Примљено 19. јуна, ревидирано 4. децембра 2002)

REFERENCES

1. J. P. Queslel, J. E. Mark, *Comprehensive Polymer Science*, Allen G., Ed. Pergamon Press, Oxford 1988,
   Vol. 2., 271-309
2. K. Dušek, M. Dušekova-Smrčkova, *Prog. Polym. Sci.* **25** (2000) 1215
3. F. Prochazka, T. Nicolai, D. Durand, *Macromolecules* **29** (1996) 2260
4. M. S. Jacović, J. Djonlagić, M. Sepulchre, M. O. Sepulchre, N. Spassky, *Makromol. Chem.* **193** (1992)
   2113
5. A. Zlatanić, B. Dunjić, J. Djonlagić, *Makromol. Chem. Phys.* **200** (1999) 2048
6. J. Djonlagić, A. Zlatanić, B. Dunjić, *Makromol. Chem. Phys.* **199** (1998) 2029
7. B. Dunjić, M. O. Sepulchre, M. Sepulchre, N. Spassky, J. Djonlagić, *Makromol. Chem. Phys.* **199** (1998)
   1051
8. H. H. Winter, F. Chambon, *J. Rheol.* **30** (1986) 367
9. P. Rempp, R. Muller, Y. Gnanou, in *Polymer Networks '91*, K. Dusek, S. I. Kuchanov, Eds., VSP, Utrecht
   1992, 25-38
10. A. Ya. Malkin, S. G. Kulichikhin, *Rheokinetics of Curing*, *Adv. Polym. Sci.* **101**, Springer-Verlag Berlin
    1991, 245
11. A. Ya. Malkin, S. G. Kulichikhin, *Rheokinetics*, *Rheological Transformation in Synthesis and Reaction of
    Oligomers and Polymers*, Hüthig&Wepf. Verlag, Heidelberg 1996.
12. Z. Petrović, J. Budinski-Simendić, T. Malavasić, W. J. MacKnight, *Polymer* **30** (1990) 1514
13. J. K. Gillham, J. A. Benci, *J. Appl. Polym. Sci.* **18** (1974) 951
14. J. M. Laza, C. A. Julian, E. Larrauri, M. Rodriqeez, L. M. Leon, *Polymer* **40** (1998) 35
15. C. W. Macosco, *Br. Polym. Sci.* **17** (1985) 239
16. H. H. Winter, P. Morganelli, F. Chambon, *Macromolecules* **21** (1988) 532
17. H. H. Winter, *Polym. Eng. Sci.* **27** (1987) 1698
18. A. Hakiki, J. E. Herz, G. Beinert, *Polymer* **33** (1992) 4574.