Kinetics of formation of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks: 2. Synthesis of the rigid network in the presence of the elastomeric network

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The kinetic aspects of the formation of a second network in the presence of the first have been studied in polyurethane–poly(methyl methacrylate) interpenetrating networks. The effect on kinetics of parameters such as the polyurethane content, the amount of acrylic crosslinker and the reaction temperature has been examined. It was found that the elastomeric polyurethane acts as a diluent that allows complete conversion of the acrylic monomers, and, through its viscosity, induces gelation of the reaction medium at the very beginning of the polymerization.

(Keywords: interpenetrating polymer networks; polyurethane; poly(methyl methacrylate); crosslinking; kinetics)

INTRODUCTION

Interprenetrating polymer networks (IPNs) present an attractive solution to the blending of two polymers[1]. Mutual entanglement prevents any further phase separation once both constituents have been crosslinked, and therefore no subsequent change in properties has to be feared. However, IPNs are quite complicated systems and only few of the usual investigation methods for polymers are suitable for studying them. As a consequence, general structure–property relationships have not yet been established, and only their synthesis and some application-oriented properties are usually reported in the literature[1]. Attempts have been made to model the formation of IPNs[2], but the results merely apply to the system under investigation and may not be generalized. On the other hand, the chemical aspects of IPN formation, i.e. the kinetics, the viscosity and the compatibility changes during polymerization, etc., have rarely been investigated. Nevertheless, it is important to understand how one network is formed in the presence of the other or of its precursors. Once the chemical system is chosen, the factors that govern the polymerization are directly responsible for the resulting morphology and properties of the material.

Amongst the various IPNs under investigation in our laboratory[3], we have chosen a very simple polyurethane–poly(methyl methacrylate) (PUR–PMMA) system for an in-depth study of the processes involved in network formation leading to IPNs. The elastomeric polyurethane (PUR) consists of an aromatic triisocyanate combined with a poly(oxypropylene) glycol. The rigid phase (PAc) is formed by methyl methacrylate copolymerized with a trimethacrylate. After mixing all the reagents, the PUR is prepared first at room temperature, followed by the acrylic constituent at 60°C. We have adopted the term '*in situ* sequential' IPNs for such materials, which emphasizes that all the reagents are introduced simultaneously in the reaction vessel, but that the networks are formed in a sequential mode.

In this paper, we report on the formation of the acrylic phase in the presence of the already formed polyurethane network. The influence of various parameters on the kinetics is examined: the PUR content, the amount of acrylic crosslinker and the temperature of the reaction medium. The main results have been obtained through Fourier transform infra-red (*FT*i.r.) spectroscopy.

EXPERIMENTAL

PUR–PAc IPNs were directly synthesized in the i.r. cell following the basic procedure described in the first paper of this series[4]. The elastomeric PUR network was prepared by reacting an aromatic triisocyanate, Desmodur L (Bayer AG), with a poly(oxypropylene) glycol (ARCO Chemical), molecular weight 2000 g mol^{-1}; the catalyst was stannous octoate (Goldschmidt). The rigid PAc network was obtained by radical copolymerization of methyl methacrylate (Merck) and trimethylolpropane trimethacrylate, TRIM (Degussa), in the presence of 2,2'-azobisisobutyronitrile, AIBN. The mixture of all reagents was injected into a cell formed by two sodium chloride plates separated by a 20 μm thick gasket. The cell, which was sealed afterwards, was fixed into a Specac heating chamber. The infra-red spectra were obtained on a Nicolet model 60SX *FT*i.r. spectrometer by averaging 32 consecutive scans with a resolution of 2 cm^{-1}. The sampling interval was 1 min during most of the reaction. Reaction conversion was calculated from the change of the normalized absorbance. The variation of the isocyanate peak (2275 cm^{-1}) was followed during PUR formation at room temperature. When the conversion ratio was over 90% (see *Figure 1*),

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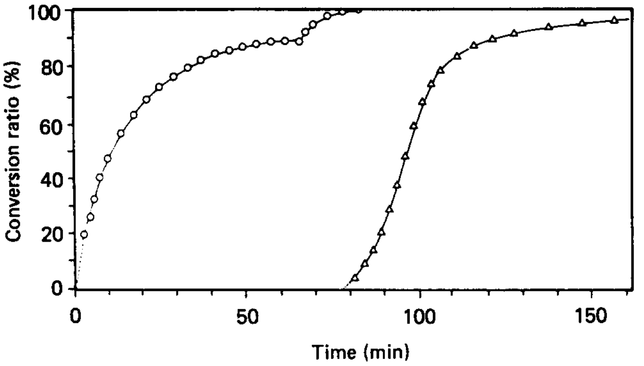

Figure 1 Conversion profiles for an IPN (25/75): PUR (○), PAc (△)

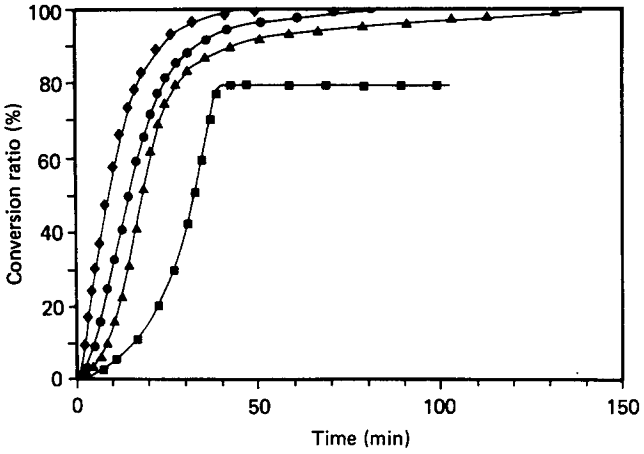

Figure 2 Conversion profiles for methyl methacrylate with TRIM copolymerization at various PUR network contents: (■), 0%; (▲), 25%; (●), 34%; (◆), 66%

the temperature was raised to initiate radical copolymerization. The C=C peak at 1639 cm^{-1}, not overlapping with its neighbours, was used to calculate the PAc conversion.

RESULTS AND DISCUSSION

In a previous paper[4], we have checked that *FT*i.r. spectroscopy is an appropriate method to follow the monomer-to-polymer conversion, and that the Beer–Lambert law remains valid in the concentration and temperature ranges used in this work. Typical conversion *versus* time curves, $P=f(t)$, for PUR and PAc are shown in *Figure 1*. The rate of polymerization, R_p, is deduced from the slope at each point of such curves. For all the parameters influencing the kinetics of the acrylic system, i.e. polyurethane content (per cent PUR), crosslink density (per cent TRIM) and temperature (T), two series of curves, $P=f(t)$ and $R_p=f(P)$, were drawn, which allows us to discuss the main features of the kinetic process.

Figures 2 and *3* show the influence of the polyurethane content. With increasing PUR from 0 to 66% by weight, the rate and the final degree of conversion both increase. At a 66% PUR content, $P=90\%$ after 20 min; without PUR, only a 15% conversion ratio is reached after the same time. The initial polymerization rate is about five times higher at 66% PUR than for the PAc system in bulk. Also, the $R_p=f(P)$ plots are very different: with a low elastomer content, the curves show a pronounced maximum, and total conversion is not obtained; on the other hand, in the 66/34 IPN, the curve is flattened and the conversion is 100%. Increasing the PUR content therefore accelerates the polymerization and leads to a higher degree of conversion of the acrylic monomers.

The effect of the acrylic crosslinker on the kinetics of the second network is described by *Figures 4* and *5* for a 34/66 IPN. As the per cent TRIM is varied from 0 to 7.5, the

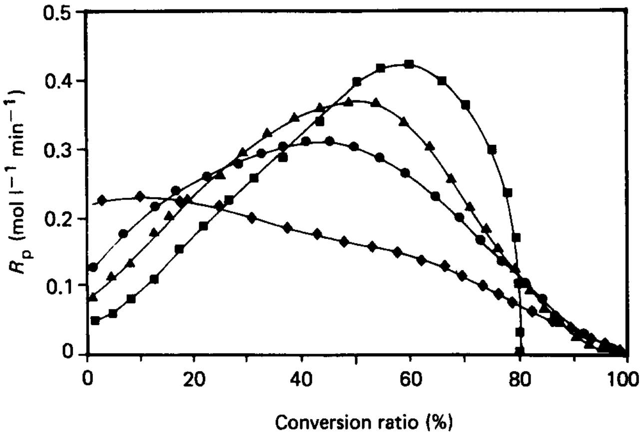

Figure 3 Rate profiles for methyl methacrylate with TRIM copolymerization at various PUR network contents: (■), 0%; (▲), 25%; (●), 34%; (◆), 66%

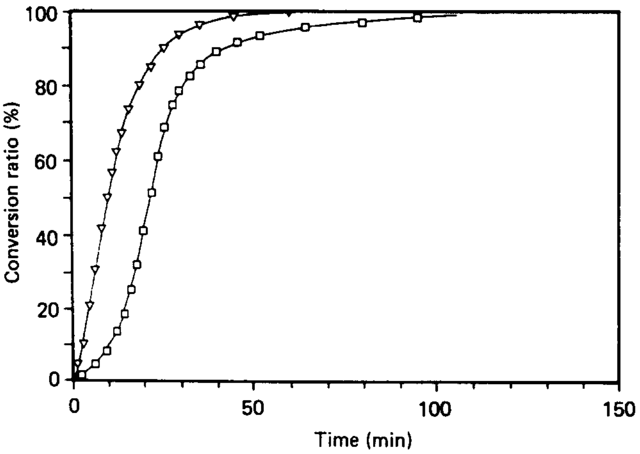

Figure 4 Conversion profiles for methyl methacrylate polymerization for a 34/66 IPN, 7.5% TRIM (▽), and for a 34/66 semi-IPN, 0% TRIM (□)

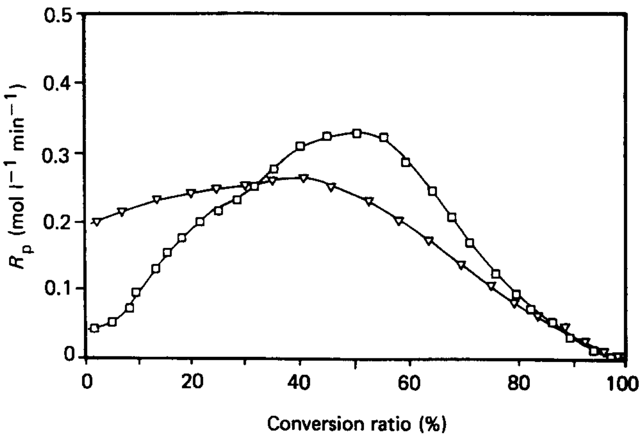

Figure 5 Rate profiles for methyl methacrylate polymerization for a 34/66 IPN, 7.5% TRIM (▽), and for a 34/66 semi-IPN, 0% TRIM (□)

Table 1 PAc final conversion ratio as a function of polyurethane content and amount of crosslinker. (Experimental conditions: temperature, 60°C; AIBN, 1 wt%)

	PUR (%)			
TRIM (%)	0	15	25	34
0	86	88	92	100
5	81	97	100	100

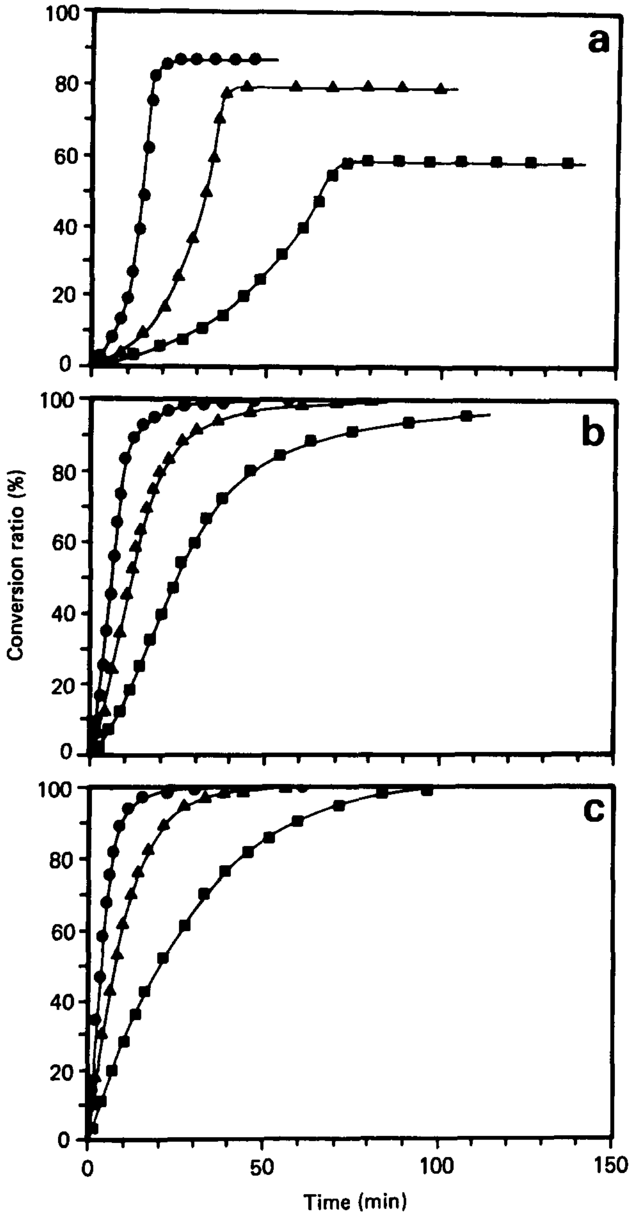

Figure 6 Influence of temperature on PAc formation. Conversion profiles in the presence of (a) 0% PUR, (b) 34% PUR and (c) 66% PUR. Temperatures: (■), 50°C; (▲), 60°C; (●), 70°C

conversion curves are shifted leftwards, showing an acceleration of the polymerization process; the initial rate is increased, but the maximum rate is lowered. Adding more crosslinker therefore causes autoacceleration at a smaller conversion and has a similar effect as an increase in the PUR content: both parameters induce an earlier onset of the Trommsdorff effect with a higher initial conversion rate.

The effect on final conversion is also almost the same (*Table 1*). As already shown, the system tends towards completion with more polyurethane. Adding TRIM to the acrylic phase allows complete polymerization at even lower PUR content, around 25%. Only in the absence of PUR is the final conversion lower for the crosslinked PAc than for the linear PMMA[5]. This observation will be discussed later.

The effect of temperature is given in *Figures 6* and *7* for IPNs containing 0, 34 and 66% PUR. Similar results are obtained for the other compositions. The temperatures under consideration correspond to our usual experimental conditions: all are below the glass transition temperature of the rigid phase (about 105°C). As may be expected, the rate of propagation and the degree of conversion increase when the temperature of the reaction medium is raised. The change in the rate profiles with the concentration of polyurethane is significant: a higher

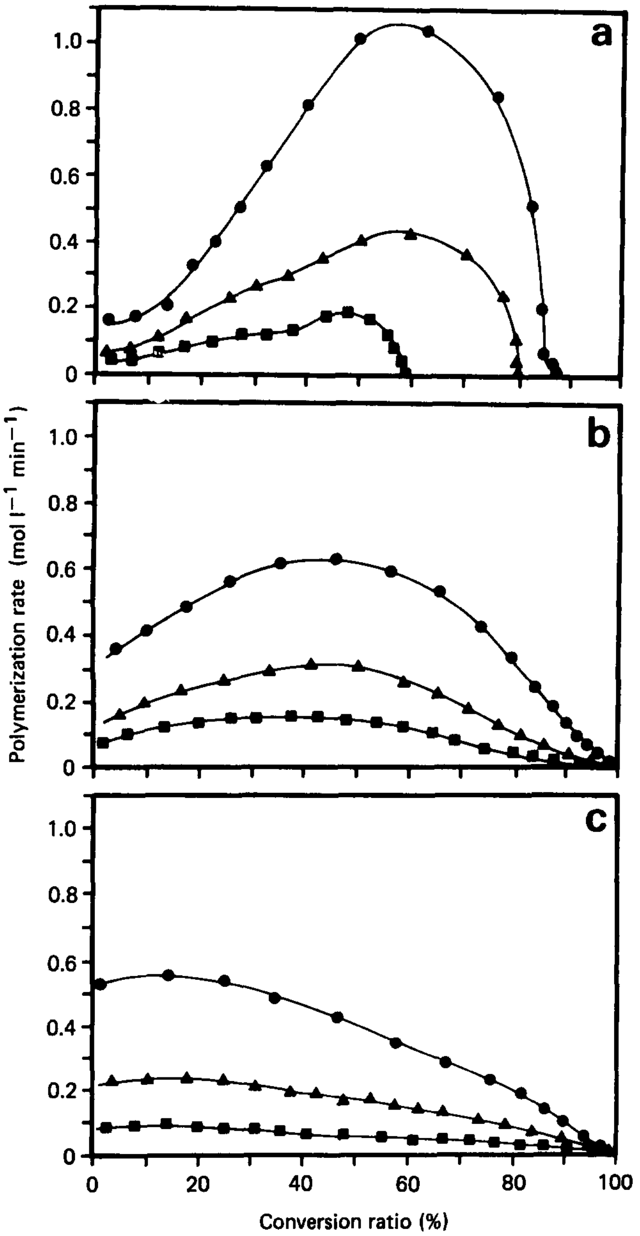

Figure 7 Influence of temperature on PAc formation. Rate profiles in the presence of (a) 0% PUR, (b) 34% PUR and (c) 66% PUR. Temperatures: (■), 50°C; (▲), 60°C; (●), 70°C

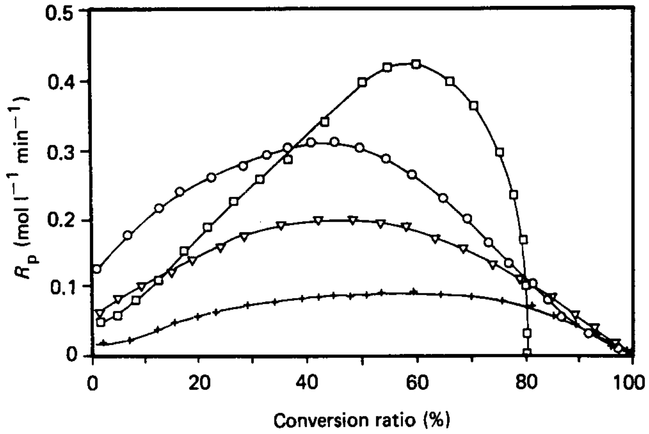

Figure 8 Rate profiles for methyl methacrylate with TRIM copolymerization in bulk (□), in solution (ethyl acetate (+) and polyol (▽)) and in presence of PUR network (○)

elastomer content shifts the maximum rate towards smaller conversion ratios.

The *P versus t* and R_p *versus P* curves shown above resemble those for radical polymerization of methyl methacrylate in bulk[6,7]: after an initiation period, the Trommsdorff effect causes an important viscosity increase of the reaction medium, the polymerization is first accelerated and then the propagation finally slows down to zero. At this point, the conversion of the monomer may not be complete, depending upon the polymerization temperature[8,9].

In *Figure 8*, the copolymerization of methyl methacrylate with TRIM in the presence of 34% PUR is compared with that in other reaction media, in bulk and in solution. The rate profile with PUR presents a maximum that is more damped than those usually encountered in bulk polymerization[6]. It seems that the polyurethane behaves rather as a diluent towards the acrylic polymerization; like with ethyl acetate or the more viscous polyol, a final conversion of 100% is reached. The presence of the elastomeric network prevents the reaction medium from attaining the glassy state exactly as a solvent would do.

As a matter of fact, the reaction medium changes from the beginning of the polymerization process to the end: first, it consists of PUR swollen by the acrylic monomers; then, as conversion proceeds, the concentration of PAc increases at the expense of the monomers. Without the presence of PUR, a limiting conversion would be observed at a given polymer/monomer ratio, depending on the polymerization temperature. As this is not the case, it follows that at least from this point on, polyurethane is necessary as a diluent for obtaining a 100% conversion.

Dynamic mechanical investigations have shown[10] that phase separation exists in the present type of PUR–PAc *in situ* sequential IPNs, even though some improved miscibility is observed. If the polymerization process leads to large glassy domains, it will be necessary that at least some radicals are on the domain border or in an interphase containing both PUR and PAc in order to be reached by the remaining monomer molecules. The presence of radicals on the elastomeric phase may be excluded, as no grafting on PUR through transfer reactions has been detected for the present system[3]. Finally, it is also possible that the combining of PUR and PAc by interpenetration causes a high mutual dispersion of the phases so that all the domains are small enough to allow monomer diffusion towards a radical, until its total consumption. Further work is necessary to settle this point, but the main result is that phase separation does not hinder the complete monomer-to-polymer conversion.

Another factor to be considered in order to explain the experimental results is the viscosity of the reaction medium: the initial rate increases as the reaction medium becomes more viscous, i.e. when going from solvent polymerization to polymerization in the presence of PUR, and the onset of the gel effect also begins at smaller conversion ratios (*Figure 8*). In that way, the PUR behaves like a viscous medium in which the acrylic polymerization proceeds. Raising the temperature shows the classical accelerating effect and needs no further comment. Of course, a temperature of the reaction medium above the glass transition temperature of the rigid constituent would allow complete conversion of the monomers even without PUR. The activation energy of the PAc system was calculated from the temperature data[5]: the value found is around 19 kcal mol^{-1} whatever the conversion ratio for crosslinked PAc as well as for all IPNs; this means that these parameters do not influence the activation process of the acrylic monomers.

Our results concerning the crosslinking of the hard phase show that the presence of TRIM interferes with that of PUR. In a classical radical crosslinking reaction in bulk[11], adding the crosslinker produces an earlier onset of the Trommsdorff effect, as well as earlier maximum rate and final stop of polymerization. According to Miller and Macosko[12] the crosslinker takes part in the polymerization in the very first steps of conversion, causing the viscosity to rise and therefore an earlier gelation of the reaction medium. The same situation is observed in the PUR–PAc IPNs, except that the value of the final conversion increases as soon as polyurethane is present (*Table 1*): the elastomer maintains the medium beyond the glassy state, and the reaction can proceed to completion. Therefore, both PUR and TRIM produce an earlier Trommsdorff effect, with a higher initial rate; but the role of PUR as a diluent allows a more even reaction rate and a final conversion ratio closer to 100%: in some way, the elastomer counterbalances the influence of the crosslinker.

For simplification purposes, the above discussion has been summarized in two schemes: in the first one (*Table 2*), the variation of the kinetic parameters in different reaction media is compared to that of polymerization in bulk; the second scheme (*Figure 9*) shows the relationship between the temperature of the reaction medium with

Table 2 Kinetic changes of the bulk polymerization of MMA induced by various components

	Addition of			
	Diluent			
	Ethyl acetate	Polyol	TRIM	PUR network
Initial rate	lowered	increased	increased	increased
Trommsdorff effect				
onset	delayed	advanced	advanced	advanced
intensity	lowered	lowered	increased	lowered
Final conversion	1	1	<1	1

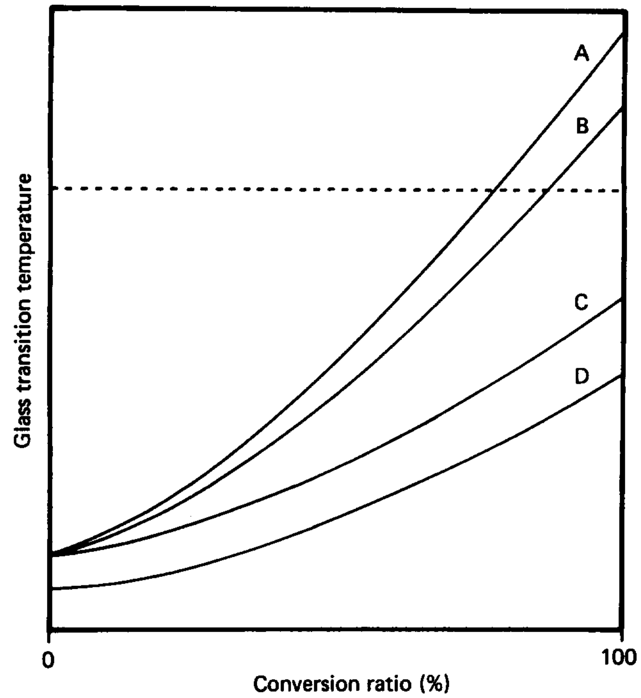

Figure 9 Relationship between conversion ratio, glass transition temperature and polymerization temperature for various systems: (A), PAc; (B), PMMA; (C), ethyl acetate/PAc; (D), PUR/PAc. Polymerization temperature is marked with horizontal broken line

regard to its glass transition temperature, and the conversion ratio. Both *Table 2* and *Figure 9* provide an easier understanding of the role of the different parameters involved in the polymerization process.

CONCLUSIONS

Polyurethane has two effects on the formation of the acrylic phase in PUR–PAc *in situ* sequential IPNs. It confers a high viscosity to the reaction medium from the very beginning of the polymerization process, inducing a high initial rate and an early gelation effect. On the other hand, polyurethane acts as a diluent which keeps the glass transition temperature of the reaction medium below the glass transition temperature of the rigid phase, therefore allowing complete monomer-to-polymer conversion.

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