Polyurethane–poly(methyl methacrylate) interpenetrating polymer networks: 1. Early steps and kinetics of network formation; intersystem grafting

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Several side-reactions occurring during the early stages of the formation of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks (PUR/PAc IPNs) have been examined. Thus, the PUR catalyst, stannous octoate, is able to initiate the polymerization of the methacrylic monomers, or to accelerate it in the presence of the proper initiator of the system, azo-bisisobutyronitrile. Nevertheless, this effect does not influence the overall reaction process. On the other hand, light has to be excluded in order to obtain transparent IPNs. The kinetics of formation of the individual networks have been investigated in experimental conditions as close as possible to the actual preparation of the corresponding IPNs. Intersystem grafting, if any, is very limited and its influence on the mechanical properties may therefore be neglected.

Keywords Polymer; interpenetrating networks; polyurethane; polyacrylic resin; side-reactions; kinetics; grafting

INTRODUCTION

Interpenetrating polymer networks (IPNs) represent an interesting approach to the problem of polymer blends. Though Millar[1] was the first to study such materials in some detail, the main contribution in this field was made by two teams, namely those of Sperling[2] and of Frisch[3]. Besides the more basic aspect of the mixing of two or more polymers, they have shown such materials to have some new or enhanced properties. Like other multicomponent systems, IPNs exhibit phase separation, which arises from the more or less marked mutual incompatibility inherent in polymers[2]. But in mechanical blends, or in block and graft copolymers, the size of the domains may fluctuate with time or applied stress, and therefore induce unwanted changes in the properties of the material. This is not possible in IPNs, where the structure is in some way 'fixed' as soon as the crosslinking of both networks has been achieved.

IPNs can be obtained in two ways[2]. In the two-step process, one network is swollen by the components of the second which are polymerized and crosslinked *in situ*. In the one-step process, all the monomers are mixed and the two networks are formed more or less simultaneously. This mode of preparation implies that the polymerization of the two systems proceeds in different ways, for example addition polymerization and polycondensation, as otherwise intersystem chemical grafting would yield materials different from IPNs where only physical entanglement is thought to exist. As the swelling of polymer networks is a rather long process, the one-step synthesis seems more suited for industrial applications. The structure of the IPNs is determined by the chemical nature of the components and by parameters such as the crosslink density and the kinetics of polymerization of each network. It is directly responsible for the different properties of the final material, and therefore a special task in preparing IPNs should be the detailed knowledge of all the reactions and side-reactions taking place during synthesis.

Amongst other polymer couples, polyurethane (PUR) and polyacrylic esters (PAc) have been combined very often as IPNs, mainly because these polymers are already widely used in the plastics industry. Various mono- or multifunctional monomers, prepolymers and catalysts are also available without problem. Frisch and coworkers[4,5] have thoroughly investigated PUR/PAc systems, which they have usually prepared by the one-step method. They have shown that the behaviour of these combinations is due to a greater interpenetration of the two component phases as compared to the corresponding mechanical blends, or the so-called semi-IPNs, where only one component is crosslinked. Allen *et al.*[6] have also studied PUR networks containing linear methacrylic polymers. They have shown that their materials have improved impact and shear resistance.

PUR/PAc IPNs or semi-IPNs have also been prepared in our laboratory for some time[7]. The first goal was an in-depth investigation of the different synthetic steps and of the parameters governing the formation of such composites. The PUR network is elastomeric and consists of an aromatic triisocyanate associated with a poly(ether) glycol; the rigid PAc network is built up from methyl methacrylate and trimethacrylate. Only the one-step synthesis mode is utilized. The PUR network is formed first, at room temperature, and then the PAc network is

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Table 1 Materials

Materials	Description	Source	Code
Polyol	Poly(oxypropylene) glycol: $\bar{M}_n$ 2000; 1.05 OH/kg; density 1.0 g ml^{-1}; viscosity 370 cP	P.C.U.K. (P 1020)	POPG
Polyisocyanate	Trimethylol-1,1,1-propane/toluene diisocyanate adduct, containing 25 wt % of ethyl acetate; 3.1 NCO/kg; density 1.17 g ml^{-1}	Bayer (L 75)	L 75
PUR catalyst	Stannous octoate: 28.5% tin; density 1.25 g ml^{-1}	Goldschmidt (KOSMOS 29)	OcSn
Acrylic monomer	Methylmethacrylate: stabilizer hydroquinone 50 ppm	Flucka	MAM
Acrylic crosslinking agent	Trimethylol-1,1,1-propane trimethacrylate: stabilizer methylhydroquinone 100 ppm; density 1.06 g ml^{-1}	Degussa (TRIM)	TRIM
Initiator	Azo-bisisobutyronitrile	Merck	AIBN
Model compound for PUR	α,ω-phenylurethane derivative of POPG: 0% NCO; viscosity 2800 cP	Our laboratory	PO[illegible]

formed by heating. Here we examine successively the following aspects of the preparation of PUR/PAc IPNs: (a) the existence of side-reactions in the early stages of the synthesis; and (b) the kinetics of network formation and the occurrence of intersystem grafting. The influence of various chemical parameters on the synthesis will be reported in a subsequent paper[8].

EXPERIMENTAL

Reagents

All the reagents are listed in *Table 1*. In some cases, the indications given by the manufacturers were verified. The isocyanate (NCO) content of the triisocyanate L 75 was controlled periodically by titration with di-n-butylamine[9]. A value of 3.0 NCO/kg (given: 3.1) was found, which remained stable over at least six months though the container was frequently opened. The molecular weight $\bar{M}_n$ of the polyether, POPG, determined by g.p.c. (Waters Associates, Styragel columns, THF) was 2100; polydispersity index was 5.5. By the phosgenation method[10], the hydroxyl (OH) content was found as 1.05 OH/kg (given: 1.05). The catalyst, stannous octoate, OcSn, contains 29.15% of tin (indicated: 28.5 ± 0.5). It is protected against oxidation by a non-identified antioxidant.

The methacrylic monomers, methyl methacrylate (MAM) and trimethylolpropane trimethacrylate (TRIM), were dried for three weeks over a 4 Å molecular sieve, as well as POPG. Their water content was checked by the K. Fischer titration method[11]. No further purification was made; especially, the inhibitor was not removed from the methacrylic monomers. As a model compound, the α,ω-phenylurethane derivative of POPG (POPUR) was prepared[12]. It was obtained by reacting POPG with the stoichiometric amount of phenylisocyanate. The reaction was followed to completion by i.r. spectroscopy (disappearance of the isocyanate, NCO, absorption peak at 2300 cm^{-1}).

Synthesis of the composites

The reagents were mixed together and rapidly stirred under dry nitrogen, stannous octoate being added last, as its catalytic action begins immediately upon contact with the PUR precursors. The end of mixing was set as the origin of the reaction times. The mixture was introduced into a mould consisting of glass plates (20×15 cm^2) separated by an elastomeric gasket (diameter 3 mm in standard conditions), and spring-loaded to follow the shrinking during polymerization. The gelation was taken as being the viscosity of the system at which a small needle could no longer penetrate the reaction medium. In standard conditions, gelation occurred after about 20 min; after 10 min more, the mould was transferred into a heating oven with a forced air circulation which allows effective temperature regulation within ± 2°C. The mould was heated up to 56°C, a temperature around which the polymerization of the methacrylic monomers is usually started. Upon completion of the reaction, the sheets were annealed (75°C for one night, and 120°C for 3 h).

Determination of the chemical composition of a PUR/PAc IPN

PUR content. This is the weight per cent (W) of PUR in the IPN: thus a 34/66 IPN contains 34 g of PUR for 100 g of IPN.

PUR network. K represents the number of isocyanate groups per hydroxyl group: $K = \mathrm{NCO/OH}$. $K = 1$ for stoichiometric conditions. The percentage of catalyst is based on the total weight of IPN:

$$\mathrm{OcSn}(\%) = \frac{W_{(\mathrm{OcSn})}}{W_{(\mathrm{IPN})}}$$

PAc network

$$\mathrm{TRIM}(\%) = \frac{W_{(\mathrm{TRIM})}}{W_{(\mathrm{MAM})} + W_{(\mathrm{TRIM})}}$$

$$\mathrm{AIBN}(\%) = \frac{W_{(\mathrm{AIBN})}}{W_{(\mathrm{MAM})} + W_{(\mathrm{TRIM})}}$$

Solvent extraction and analysis of the soluble extract

The soluble components in the various IPNs were extracted in a Soxhlet apparatus with ethyl acetate. Usually, after 70 h of refluxing, no more extract was released. The i.r. analysis of the soluble species was carried out on a Perkin–Elmer Model 225 spectrometer. First, a calibration curve was set up[13]: for example, for the determination of the amount of POPUR extracted from PAc networks (*Table 10*), the NH absorption peak at 3300

Table 2 Addition of different reagents of the acrylic system to PUR precursors

PUR precursors containing	Appearance of turbidity (min)	Time to gel (min)	Aspect of gel
Ethyl acetate	none	12–15	transparent
MAM + TRIM	none	15	transparent
Ethyl acetate + AIBN	none	15	transparent
MAM + TRIM + AIBN	6–8	15–20	milky

Room temperature; for composition, see text

Table 3 Addition of different reagents of the PUR system to the PAc precursors

PAc precursors, containing	Appearance of turbidity (min)	Time to gel (min)	Aspect of reaction medium
No additive	none	>180*	transparent liquid
L 75	none	>180*	transparent liquid
POPG	180	>180*	milky liquid
OcSn	none	30	transparent gel
POPG + L 75	45	>180*	milky liquid
POPG + OcSn	20	42	milky gel
L 75 + OcSn	none	30	transparent gel

Room temperature; for composition, see text
* 3 h = maximum observation period

cm^{-1} was chosen and measured for various POPUR/MAM mixtures[12].

RESULTS AND DISCUSSION

If not otherwise stated, the reaction mixtures under investigation always had the following compositions by weight: 34% PUR containing the stoichiometric amounts of L 75 and POPG. The acrylic phase was composed of 95% MAM, 5% TRIM and 2% AIBN[7]. The OcSn content (1.45%) was based on the total weight of the mixture (i.e. not only on the PUR content). Ethyl acetate is a good solvent for all the reagents and was used instead of MAM for comparison.

Early reaction steps

The reaction medium contains three reagents for each system, some of which are quite reactive. Thus the system as a whole is very complex and some unwanted side-reactions may occur which could seriously hinder or change the course of network formation. A first series of tests was made at room temperature and did not exclude light. Then, the influence of the latter was examined, mainly because of the sensitivity of the acrylic system to photoinitiation[14]. For each mixture, we have noted the appearance of turbidity, the gelation time and the aspect of the gel. The maximum observation time did not exceed 3 h.

The successive addition of the different reagents to the reaction flask does not cause any cloudiness or precipitation; the mixture also remains transparent and homogeneous during its transfer into the mould, so that no incompatibility exists so far. The mixtures in *Table 2* contain the precursors and the catalyst of the PUR system to which either ethyl acetate (as a reference medium) or the components of the PAc system are added. In all cases the gelation of PUR occurs; it usually takes 15 to 20 min. Thus, the methacrylic monomers do not notably influence the kinetics of PUR formation as compared with ethyl acetate. All the gels but one are transparent: only in the presence of the whole PAc system does a permanent white turbidity appear after 6 min. As light has not been excluded, the polymerization of the methacrylic monomers may well be initiated, the AIBN acting as a photosensitizer[14]. This result indicates that, contrary to its monomer, PMMA is not soluble in one of the precursors of the PUR system.

In a second set of tests, the different PUR presursors have been added successively to the PAc system, i.e. MAM + TRIM + AIBN. *Table 3* does not show any effect due to isocyanate: the medium remains transparent, without gelation. Furthermore, turbidity appears only when POPG is present but, as the initial mixture is water-clear, only the formation of another polymeric species such as PMMA may explain the observed turbidity. The latter appears faster when L 75 or OcSn are present together with POPG. But only in the latter case (POPG + OcSn) is a gel formed. From *Table 3* it also appears that the PAc system is able to gel at room temperature upon addition of OcSn, so that the PUR catalyst clearly interferes in the acrylic polymerization process. Thus it has to be established whether AIBN and OcSn can be utilized together for the formation of PUR/PAc IPNs, or not.

The above results also led us to examine the effect of light on the polymerization of the methacrylic monomers, in the presence or absence of OcSn. *Table 4* shows that the tin catalyst is able to induce polymerization, even without AIBN: with light, a transparent gel is formed in about 80 min. When AIBN and OcSn are both present in the monomer mixture, a notable acceleration leads to transparent gels even in darkness.

The results summarized in *Tables 2* to *4* have shown some unexpected reactions: (a) POPG precipitates in the presence of PMMA, giving a white turbidity; and (b) the PUR catalyst, alone or associated with AIBN, influences the radical polymerization of the acrylic system, this effect being more pronounced in the presence of light.

The incompatibility of POPG and PMMA has been confirmed by adding the diol to a solution of PMMA: precipitation occurs immediately. Obviously, the molecular weight plays a role and, for example, the same POPG with $\bar{M}_n \sim 400$ only does not precipitate[12]. Comparison of the solubility parameters of the different

Table 4 Effect of the PUR catalyst (OcSn) on the acrylic system in the presence or absence of light

	With light		Without light	
Composition of mixture	Time to gel (min)	Aspect of reaction medium	Time to gel (min)	Aspect of reaction medium
MAM + TRIM	no gel	transparent liquid	no gel	transparent liquid
MAM + TRIM + AIBN	>180	transparent liquid	no gel	transparent liquid
MAM + TRIM + OcSn	80	transparent gel	no gel	transparent liquid
MAM + TRIM + OcSn + AIBN	30	transparent gel	60	transparent gel

Room temperature; composition, 5% TRIM, 95% MAM, 2% OcSn, 2% AIBN

Table 5 Solubility parameters of various compounds used in the preparation of PUR/PAc IPNs

	Solubility parameters	
Compound	As found	Literature[c]
Ethyl acetate	–	9.1
MMA	8.9[a]	8.8–8.9
PMMA	9.2[a]	9.1–9.5
POPG (P 1020)	7.7[a]	–
PUR	9.4[b]	9–10

[a] Calculated according to Small[15]
[b] Determined by the swelling method[16]
[c] Ref. 17

species (*Table 5*) shows that only PMMA and POPG have very differing values, whereas those of PUR and PMMA are quite close. Therefore, the appearance of turbidity results rather from a lower degree of dispersion of POPG, i.e. when several molecules of diol have the opportunity to assemble and thus to segregate in the acrylic medium. This implies that the polymerization of the methacrylic monomers should only begin when POPG has been more or less completely integrated into the PUR network. Therefore, the 'quality' of the latter appears as an essential condition for obtaining transparent IPNs. This point will be discussed in detail again later.

The influence of OcSn in radical polymerization has not yet been examined in the literature. We have observed two quite distinct effects: the PUR catalyst is able to induce the polymerization of acrylic monomers, and radical polymerization is accelerated when the proper initiator, AIBN, is present in the reaction medium. Both reactions are still under examination; only details in relation to the preparation of PUR/PAc IPNs are reported below. In order to study the effect of only the OcSn, we have prepared a 2% solution of this reagent in MAM (about 5×10^{-3} mole OcSn per mole of MAM).

This solution precipitates in methanol where the OcSn is insoluble. But 15 min after the preparation of the solution, the amount of precipitate decreases until it disappears completely after 5 min more. Note that, when MAM is replaced by ethyl acetate, a precipitate always forms, which indicates that the double bond in MAM must play some role: a similar effect has been reported without details[18], but the presence of a hydroxyl functional was said to be necessary, which is not the case in our experiment. Nevertheless, the main conclusion is that the interaction between OcSn and MAM is slow: even when some of the catalyst is abstracted from PUR formation, its concentration remains high enough to allow gelation in 15 to 20 min, which is also the gelation time in ethyl acetate. This experiment also shows that the new species formed between MAM and OcSn is actually not responsible for the initiation of radical polymerization, as no PMMA is formed even when the contact time between MAM and OcSn is prolonged to several hours.

Note that the situation described above never arises in our system, which contains always AIBN. OcSn is a catalyst and may therefore be expected to be present in its initial form at the end of the catalysis of PUR formation. Up to now, investigations on the accelerating effect of OcSn have led to the elimination of several possible hypotheses, which we report without further comment: the decomposition rate of AIBN is not faster in the presence of OcSn; new catalytic species of either ionic or radical nature are not created; OcSn does not neutralize the inhibitor molecules existing in the methacrylic monomers and hereby shorten the induction period. Another possible reaction is being examined: as the instantaneous concentration of free radicals is always low compared to the concentration of OcSn molecules, the Sn cation could act as a radical stabilizer. In this case, the rate of deactivation by transfer would decrease, thus increasing both propagation and termination rates. Whatever the result, it is obvious that OcSn has no influence other than an accelerating effect, and that it is therefore not perturbing the system.

Kinetics of the individual networks

The preparation of PUR or PAc networks has been described quite often in the literature. Thus, only aspects concerned with their synthesis as a component of the IPN are considered here.

Polyurethane network. The PUR network forms as well in methacrylic monomers as in ethyl acetate (*Table 2*). In order to avoid an incidental polymerization of the methacrylic monomers, this solvent was preferred; it has since been established that the results also apply when the mixture of methacrylic monomers is the reaction medium. The time to reach the gel point, t_{gel}, was examined as a function of the temperature and the concentration of catalyst. The results are summarized in *Table 6*. In the present experimental conditions, PUR gelation is not observed to be exothermal; this is probably due to dilution by the solvent. *Figure 1* shows that, above a catalyst concentration corresponding roughly to $C_0/2$, the system is no longer accelerated. The usual concentration of C_0 thus appears too high, but it is justified by the role played by OcSn towards the methacrylic monomers: the interaction between OcSn and MAM may lead in fact to an actual catalyst concentration which is lower than C_0. If for some special application a higher rate of gel formation at room temperature was necessary, OcSn could still be used, but in combination with a tertiary amine[19]. However, a too fast reaction does not favour the complete formation of the polymer network[20], so that no attempt was made to decrease the gel time further. In turn, for concentrations below $C_0/2$, a large variation of t_{gel}, from 25 min to 6 h, is possible. The catalytic action is also accelerated by heating, but the saturation effect at higher concentrations is observed again: the acceleration is more pronounced for $C_0/4$ than for C_0. The gelation time is the same for C_0 at 18°C and for $C_0/16$ at 56°C. These results show that, with the usual concentration of OcSn (C_0), the gelation of the PUR component is achieved before the

Table 6 Time to gel for the polyurethane network in ethyl acetate as a function of catalyst concentration, at various temperatures

OcSn content (%)*	t_{gel} (min)			
	18°C	30°C	42°C	56°C
C_0	21	17	13	<9
$C_0/2$	25	–	–	9
$C_0/4$	45	23	15	10.5
$C_0/8$	185	–	–	15
$C_0/16$	365	–	–	21

*C_0 = 1.45%

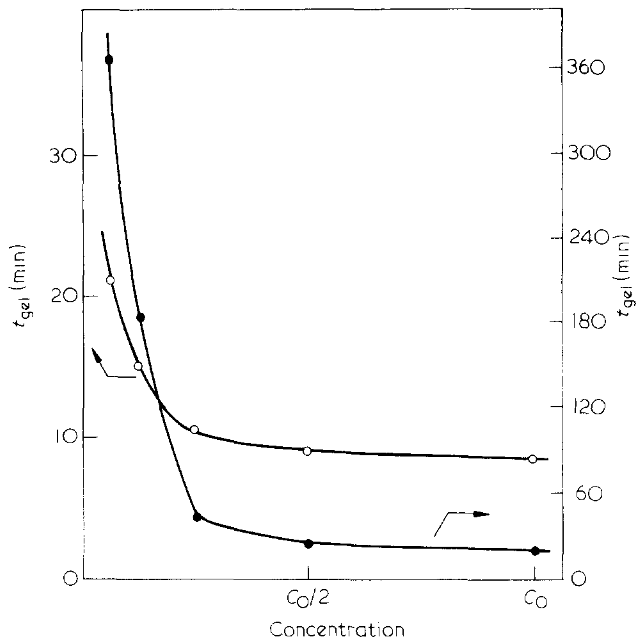


Figure 1 Time to gel for the polyurethane network in ethyl acetate ***versus*** catalyst concentration, at various temperatures: ○, $t = 56°C$; ●, $t = 18°C$

Table 7 Time to gel for PUR network, at various concentrations in ethyl acetate and methyl methacrylate

PUR content (%)	t_{gel} (min) Ethyl acetate (18°C)	Ethyl acetate (56°C)	MAM (18°C)
5	∞	∞	∞
15	100	16	100
34	21	9	22

mould is heated up in order to initiate the polymerization of the methacrylic phase. Successive titrations of the remaining isocyanate groups up to the moment at which the viscosity of the medium impedes further analysis indicate that 69% of the initial NCO has disappeared, a value which corresponds to the calculated one[14].

Table 7 shows the variation of gelation time with PUR content. When the concentration of the PUR precursors in the reaction medium is too low (5%), the network cannot form. This result has also been noted by others[21]; it does not exclude the formation of linear or grafted macromolecules, or even the presence of small gel zones in the medium. As by definition the concentration in OcSn is always C_0, its actual concentration is about 7 times higher in the 5% solution than in the 34% dilution. This confirms the existence of an upper catalyst concentration above which no further acceleration of the system is possible. Thus, it is clear that the faster gelation is only due to the higher probability of encounter between the isocyanate and the glycol molecules. As expected, increasing the temperature lowers t_{gel}. *Table 7* indicates also that, when ethyl acetate is replaced by MAM, the gelation times are not affected; it is therefore possible to apply the above results to the PUR/PAc system.

Polymethacrylic network. The radical polymerization, mainly in highly concentrated solutions or in the bulk, starts slowly but at a given, usually low, conversion, autoacceleration leads to a large rise in temperature and to a rapid gelation of the reaction medium[14]. A typical time/temperature curve is given in *Figure 2*. Usually, complete hardening takes place quite close to the gel point and t_{max}, the time corresponding to the maximum of the exothermic peak, has been noted instead of t_{gel}, as it is more accurate.

Three parameters concerning the kinetic behaviour of the formation of PAc networks have been considered: the influence of OcSn, the dilution, and the amount of crosslinking agent (TRIM).

Role of OcSn. The accelerating effect of OcSn on the formation of the PAc network already described is detailed here. Two mixtures of methacrylic monomers, MAM + TRIM, are prepared, one containing only AIBN (2%) and the other in addition OcSn (1.45%). Both moulds are heated as usual up to 56°C, the temperature at which a small exothermal change indicates the onset of radical polymerization. In *Figure 2* and *Table 8*, it can be seen that the reaction rate is slower in the absence of OcSn. Nevertheless, the same quantity of heat is released in both cases, as shown by the evaluation of the areas under the time/temperature curves, which are identical within experimental error. Thus, OcSn does not affect the conversion of monomer to polymer, but influences only the polymerization rate of the acrylic system.

Effect of dilution. The mixture of methacrylic monomers was diluted by various amounts of POPG used in the

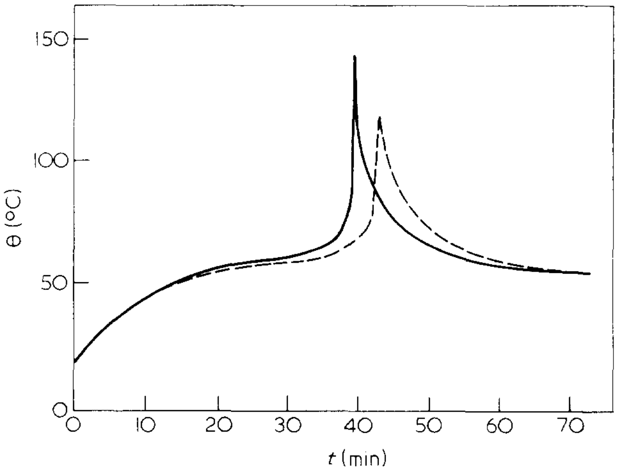


Figure 2 Time ***versus*** temperature curves of the bulk copolymerization of the polymethacrylic network: ——— AIBN + OcSn (area 1); – – – – AIBN (area 1.04). Areas determined with the baseline 56°C, in arbitrary units

Table 8 Time to reach the maximum of the exothermic peak for polymethacrylic networks at various dilutions

POPG (%) in PAc network	t_{max} (min) AIBN	AIBN + OcSn
0	24	20
0*	21	20
5	25	19
30	53	17

AIBN, 2%; OcSn, 1.45%

* Methacrylic monomers freed from inhibitor

Table 9 Bulk copolymerization of MAM + TRIM: time to reach the maximum of the exothermic peak versus TRIM, at various AIBN contents (Results in minutes)

	Time (min)		
AIBN (%)	2% TRIM	5% TRIM	7% TRIM
1	65	57	51
1.5	41	37	36
2	31	24	21

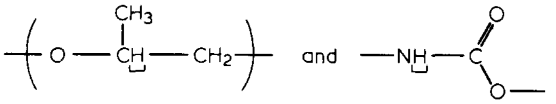
PUR network. The corresponding t_{max} appear in *Table 8*. At zero dilution, the system with OcSn is nearly 20% faster than the one containing only AIBN. As the methacrylic monomers are usually not freed from inhibitor, it seemed interesting to check whether destabilized monomers would behave differently. It appears that, when only AIBN is present, the retardation effect is decreased notably, but that there is no effect when both AIBN and OcSn are present. The experiment indicates that OcSn does not have a neutralizing influence on the inhibitor molecules, which would be responsible for the acceleration of acrylic polymerization. Another consequence is that it is not necessary to remove the inhibitor in the present system. With increasing dilution, t_{max} increases in the reaction medium containing only AIBN: this may be explained by the lower probability of encounter, but some deactivation of the radicals by POPG cannot be excluded. In the presence of OcSn, the effect of dilution on the polymerization rate is small. It is possible that, in this case, OcSn interacts with the hydroxyl group of POPG: such a reaction has been put forward as a possible mechanism in the catalysis of PUR formation by organometallic compounds[22]. The POPG/OcSn complex formed would transfer fewer radicals than POPG with its hydroxyl groups. Their mean concentration in the reaction medium would be higher, thereby accelerating the polymerization. The problem is still under examination with the use of solvents which do not transfer. But it should be kept in mind that, even in the absence of POPG, an acceleration is observed, so that several factors may be responsible rather than only one.

Effect of amount of acrylic crosslinking agent. The effect of various percentages of TRIM on t_{max} appears in *Table 9* for several AIBN concentrations. Increasing the amount of TRIM gives higher polymerization rates as more active sites, i.e. double bonds, are present[23]. It is well known that introducing more AIBN has the same effect, as the concentration of radicals in the reaction medium is higher. As already indicated for the PUR networks, a too fast polymerization is also unfavourable for PAc networks: it leads to brittle materials with irregular surfaces and, at a molecular level, to structures with a high number of pendent chains. Thus, IPNs with more than 7% TRIM or 2% AIBN have not been prepared.

Internetwork grafting

Transfer reactions cannot usually be avoided in a system where radicals are present; however, only transfer reactions leading to grafting on the PUR component of the IPNs are of importance, as they may influence the properties of the material.

Supposing that all the reagents of the PUR system have been integrated into the network, the growing methacrylic radical species is in a reaction medium that contains oxypropylene and urethane groups, with the following formulae:



$$-\!\left(O-\underset{\llcorner\!\lrcorner}{\overset{CH_3}{\overset{|}{CH}}}-CH_2\right)\!- \quad \text{and} \quad -\underset{\llcorner\!\lrcorner}{NH}-C\!\begin{array}{l}\nearrow O\\ \searrow O-\end{array}$$

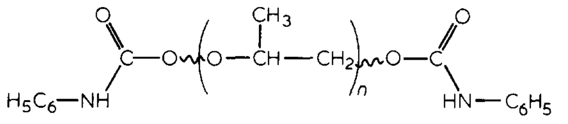
In both groups, there exists a labile hydrogen atom which may be abstracted by a radical. The possible transfer reactions resulting in a fixation onto the PUR network can be schematized as follows:

step 1: transfer by hydrogen abstraction
$Ac^* + T \rightarrow Ac + T^*$

step 2: action of the new radical, T^*
(a) $T^* + Ac \rightarrow T\sim\sim Ac^*$
(b) $T^* + Ac^* \rightarrow T\sim\sim Ac$

where Ac = acrylic mono/polymer species; T = species containing oxypropylene and/or urethane groups; Ac*, T* = corresponding activated species. When reactions like 2(a) and 2(b) actually occur, a chemical bond between PUR and PAc is created.

In order to estimate the importance of such grafting reactions, the α,ω-phenylurethane adduct of POPG (POPUR) has been prepared. It contains both the oxypropylene and the urethane groups present in the PUR:



In the experimental conditions described above, the mixture of methacrylic monomers containing various amounts of POPUR is polymerized and the resulting materials solvent-extracted and analysed by i.r. spectroscopy. Therefore an evaluation of the extent of intersystem coupling reactions is possible by estimating the POPUR percentage actually extracted. *Table 10* shows the mean values obtained from at least three extraction experiments for each sample: for the various dilutions, more than 90% of the POPUR is extracted. It is possible to make a rough evaluation of the maximal number of possible graftings per gram of PAc network. Thus, for example, the composite with 20% filler contains after solvent extraction 1.5 g (1.8%) of POPUR, or 1.5/2400 molecules of POPUR ($\bar{M}_n = 2400$), in 80 g of PAc. By assuming only one graft per molecule of POPUR, one finds 7×10^{-6} grafts per gram of PAc. The other values are listed in *Table 10*. It can be seen that these

Table 10 Determination of the soluble extract of polymethacrylic networks filled with POPUR

POPUR (%) in PAc	Optical density of sol	POPUR extracted / POPUR total (%)	POPUR (%) in PAc after extraction	Max. number of graftings per gram of PAc
20	0.24	92.5	1.8	7×10^{-6}
10	0.12	91.3	1.0	4×10^{-6}
5	0.07	90.0	0.5	2×10^{-6}

values, all around 10^{-6}, are very low, so that even when intersystem bonding occurs, its influence on a macroscopic scale is negligible.

Several works on similar systems have appeared in the literature: Klempner[24], hydrolysing PUR/PAc IPNs, was able to separate quantitatively both phases. Allen *et al.*[25] have not detected any intersystem grafting in PUR/PMMA semi-IPNs. While both studies have utilized i.r. analysis where an error of 5–10% is common, Allen has further characterized the extracts by more accurate methods (g.p.c. and n.m.r.), thereby confirming his i.r. results. Furthermore, the abstraction of the labile hydrogen from the urethane group requires strong bases[26]. On the other hand, Kahrs[27] has grafted poly(vinyl acetate) onto polyethers, in similar experimental conditions: oxyethylene glycols are more efficient than oxypropylene glycols. This author has not examined the grafting of PMMA, which in any case should be more difficult, as the chain transfer constant of the vinyl acetate radical is 10^2–10^4 times higher than that of the MAM radical[14]. Finally, in composites where grafting cannot occur (PS networks containing SIS copolymers), the complete extraction of the filler is not always possible; it depends on the pore size of the network as well as on the molecular weight of the linear polymer[28].

It will therefore be found in the forthcoming work on PUR/PAc IPNs that intersystem grafting, when it exists, is negligible in such composites and thus will not be taken into account when property/structure relationships are discussed.

CONCLUSION

A system containing all the reagents necessary to form two distinct polymer networks in the same reaction medium is inevitably quite complicated. Before undertaking property or structure studies, the possible unwanted reactions have to be investigated, as they could perturb or even prevent the formation of one or both networks. We have shown several unexpected effects to occur, like the incompatibility of PMMA and the POPG used in this study, which is likely to perturb the preparation of PUR/PAc IPNs by giving non-transparent materials: consequently, the PUR network should be formed quickly and in any case before the polymerization of methacrylic monomers begins. Also light should be excluded.

The polymerization of the PAc system may be initiated by the PUR catalyst, and is accelerated in the presence of AIBN. Another effect is the relative insensitivity of the PAc kinetics towards the dilution and the inhibitor content, when OcSn is present in the reaction medium. The formation of the PUR network is not perturbed in the acrylic reaction medium. Finally, the study of possible transfer reactions has allowed us to set an upper limit on the occurrence of internetwork graftings, while other works have established their complete absence. Their possible influence on the properties of IPNs may therefore be neglected.

These preliminary investigations have resulted in a general preparation scheme which is well adapted to the system under investigation. In a subsequent paper[8], the synthesis of PUR/PAc IPNs according to this scheme, and the role of various synthetic parameters, will be examined and some physical properties will be given.

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