Kinetics of formation of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks by Fourier transform infra-red spectroscopy: 1. Preliminary investigations

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Fourier transform infra-red spectroscopy (*FT*i.r.) was used to follow the kinetics of formation of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks (PUR/PAc IPNs). In this study, the validity of the Beer–Lambert law for the present system was checked, and its limits determined. The synthesis of the individual networks, PUR and PAc, was studied by measuring the decrease of a characteristic absorption peak of each system. A first brief example of the application of this method to a PUR/PAc IPN is given.

(Keywords: interpenetrating polymer network; polyurethane; polyacrylic network; kinetics; *FT*i.r.)

INTRODUCTION

Interpenetrating polymer networks (IPNs) of various chemical nature have been studied by several laboratories over the last few years[1]. These materials constitute a new approach to the problem of mutual incompatibility of polymers, as both components are intimately combined in their network form. It follows that the morphology of IPNs is in some way 'fixed' as soon as all the chemical reactions have taken place. It will not be changed by external stresses or by temperature as in mechanical blends or in graft and block copolymers.

Apart from this important advantage, several authors[2,3] have claimed new or at least enhanced mechanical or other properties for these materials. However, the imbrication of the two networks yields complicated morphologies, which are very difficult to investigate: IPNs are in the solid state and insoluble, so that most of the usual investigation methods cannot be utilized, or give results that are difficult to interpret.

However, before testing the IPN, a thorough chemical study of its formation is necessary, as many parameters play a role in the synthesis of such materials, for example, the more or less simultaneous formation of one network in the presence of the other and the changes of viscosity and of the degree of incompatibility during the reaction. These factors are responsible for the structure of an IPN, and therefore for its properties. But here too, the usual methods of investigation are not completely satisfactory.

Fourier transform infra-red spectroscopy (*FT*i.r.) is a rather new tool for such a study: a chemical reaction may be followed from its onset to complete conversion, even when a network is formed[4,5]. The only prerequisite is the existence of a characteristic absorption peak that follows the Beer–Lambert law and may be related accurately to the actual monomer content of the reaction medium.

We have applied this method to the polyurethane–poly(methyl methacrylate) (PUR/PAc)IPNs, which have been studied in our laboratory for some time. 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 trimethylolpropane trimethacrylate. The one-step synthesis mode is utilized; the PUR network is formed first at room temperature and then the PAc is formed by heating[6–8].

In this paper, we report preliminary studies which show that *FT*i.r. spectroscopy is an appropriate method for such a system. The validity of the Beer–Lambert law has been tested with regard to the temperature and concentration ranges used; the effect of a variation of the sample thickness on the results has also been examined. The spectra of IPN films made either directly in the i.r. cell or obtained in the usual laboratory mould are identical. Finally, a brief investigation of the kinetics of the individual networks and of a 34/66 IPN by the *FT*i.r. method is presented.

EXPERIMENTAL

Reagents and synthesis

An overview of the various materials is given in *Table 1*. Their detailed description and the determination of the compositional parameters have appeared in previous papers[6–8]. When necessary, functional and other analyses were carried out to check the indications given by the manufacturers. Water traces were eliminated, whereas the methacrylic monomers were not freed from the inhibitor molecules. A standard synthesis proceeds as follows: the calculated amounts of the various reagents are mixed and stirred thoroughly in a dry nitrogen atmosphere for a few

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minutes. The blend is poured into a glass mould. The PUR network is formed first at room temperature, and without noticeable exothermy. Thirty minutes after complete mixing of the reagents (taken as the origin of reaction times), the mould is transferred into a heating oven at 60°C where the radical copolymerization of the PAc phase is initiated. A forced air circulation in the oven allows an effective temperature regulation within ±2°C. After 1 h at 60°C, the temperature is raised to 75°C for a further 2 h.

For i.r. experiments, the above blend was injected in a cell formed by two NaCl windows separated by a Teflon gasket (around 20 μm). In one of the windows, a thermocouple may be introduced. The cell was fixed into a Specac heating chamber subject to the temperature cycle described above (accuracy ±0.5°C).

I.r. spectroscopy

The infra-red spectra were obtained on a Nicolet 60 SX Fourier transform spectrometer, by averaging 32 scans, with a resolution of 2 cm^{-1}. One spectrum was recorded every 2 min during the formation of the networks.

RESULTS AND DISCUSSION

The use of the Beer–Lambert law allows the determination of the concentration of an absorbing species through absorbance measurements. It can be expressed as:

$$A = \varepsilon c l$$

where A is the absorbance, ε is the molar extinction coefficient, c is the concentration of the absorbing molecule, and l is the thickness of the test sample.

The conversion of a monomer to its polymer may be followed by absorbance measurements if the process involves the variation of a characteristic absorption peak. The applicability of the Beer–Lambert law to the present system is examined hereafter.

Determination of the molar extinction coefficients for PUR and PAc

The isocyanate, NCO, absorption band at 2275.5 cm^{-1} was chosen for the PUR system, and the C=C peak at 1639 cm^{-1} for the PAc system. Neither band is overlapping with its neighbours, and both show a gradual decrease as the respective polymerizations proceed (*Figure 1*). *Figure 2*, where the absorbance is plotted against the concentration, shows that for both peaks the Beer–Lambert law is followed up to a given concentration: 1.7×10^{-4} mol ml^{-1} for the triisocyanate molecule, and 10^{-2} mol ml^{-1} for the acrylic monomer (cell thickness = 25 μm).

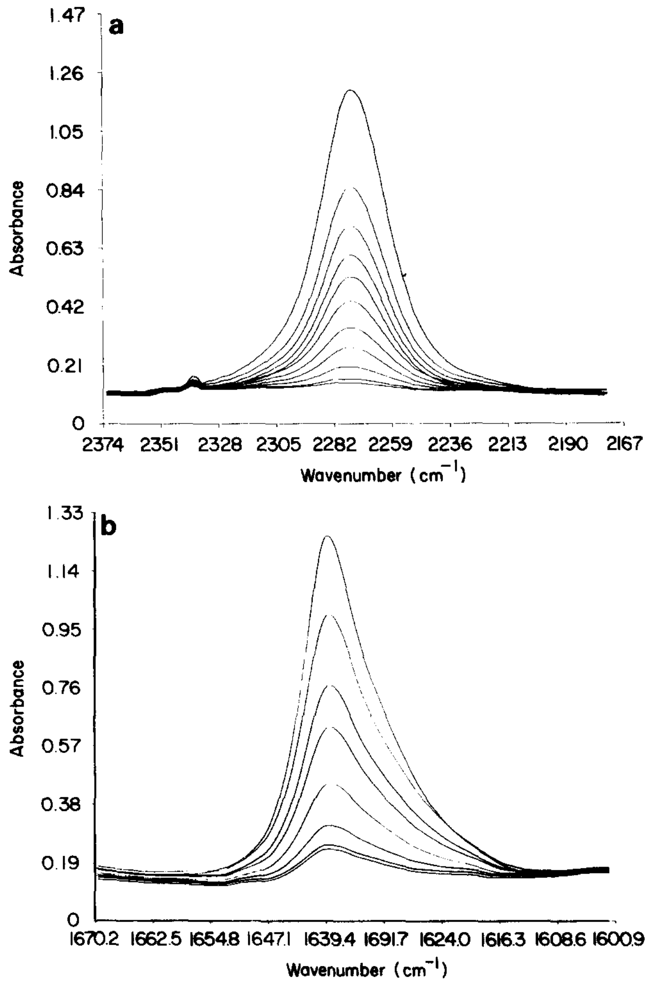

Figure 1 Decrease of a characteristic peak absorbance for (a) the PUR system (NCO) and (b) the PAc system (C=C) during polymerization

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)	OsSn
Acrylic monomer	Methylmethacrylate: stabilizer hydroquinone 50 ppm	Fluka	MAM
Acrylic crosslinking agent	Trimethylol-1,1,1-propane trimethacrylate: stabilizer methylhydroquinone 100 ppm; density 1.06 g ml^{-1}	Degussa (TRIM)	TRIM
Initiator	Azobisisobutyronitrile	Merck	AIBN
Model compound for PUR	α,ω-Phenylurethane derivative of POPG: 0% NCO; viscosity 2800 cP	Our laboratory	POPUR

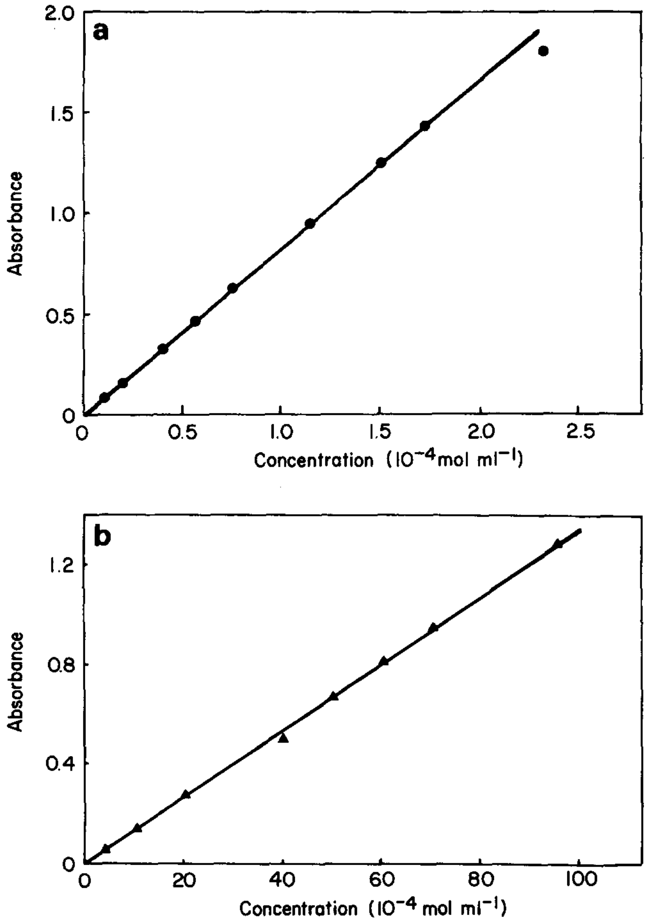

Figure 2 (a) NCO absorbance and (b) C=C absorbance as functions of concentration

The latter concentration covers the whole range of acrylic content in the IPN. However, depending on sample thickness (16, 20 or 25 μm), the law applies for IPNs with a PUR content of 92%, 78% or 60% respectively.

Furthermore, the molar extinction coefficient depends on temperature according to the relationship[9]:

$$\varepsilon=\varepsilon_0+\alpha(T-T_0)$$

where ε_0 is the value of ε at the reference temperature T_0, and α a negative constant.

As the temperature changes during the synthesis of the IPN, the molar extinction coefficient may vary. From *Figure 3*, where the variations of ε are plotted against temperature of both systems, the values of α have been determined as

$$\alpha_{NCO}=-0.0033\varepsilon_0(NCO)/deg$$

$$\alpha_{C=C}=-0.0023\varepsilon_0(C{=}C)/deg$$

These values agree with those reported in the literature[9], which are always around $0.003\varepsilon_0$/degree.

Influence of the sample thickness

The sample thickness should be known quite precisely in order to avoid important errors in the concentration, mainly when very thin samples are examined. It was measured from the interference fringes arising from multiple reflections between the internal surfaces of the cell windows (*Figure 4*). The distance l is calculated by the relationship[10]:

$$l=\frac{n}{2(\bar{\nu}_2-\bar{\nu}_1)}$$

where n is the number of maxima between the wavenumber values $\bar{\nu}_1$ and $\bar{\nu}_2$. In a series of experiments, the thickness has changed between 16 and 25 μm, corresponding to a nearly 36% variation, so that the actual thickness has to be measured in each experiment.

Determination of the degree of monomer–polymer conversion

The measure of c, the concentration of the absorbing species, through the Beer–Lambert law allows the determination of the degree of conversion P:

$$P=\frac{C_0-C}{C_0}$$

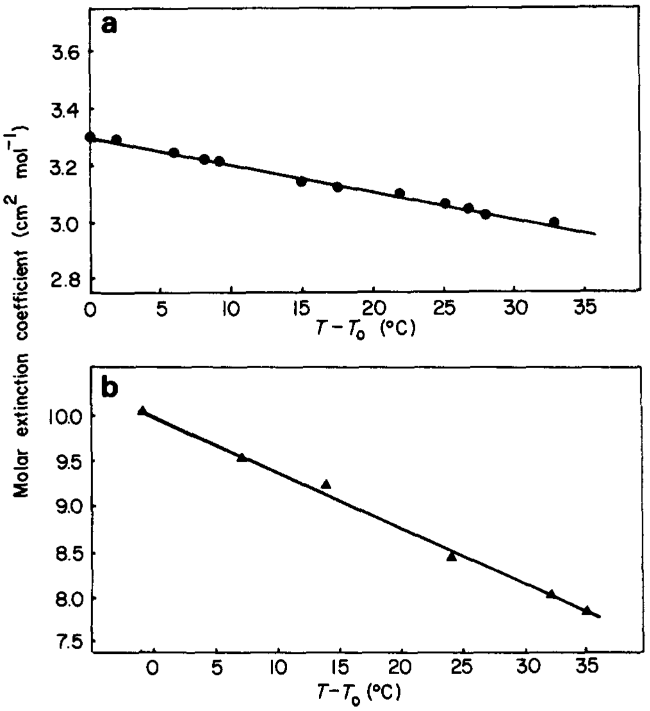

Figure 3 Molar extinction coefficients of (a) NCO and (b) C=C as functions of relative temperature ($T-T_0$); $T_0=25$°C

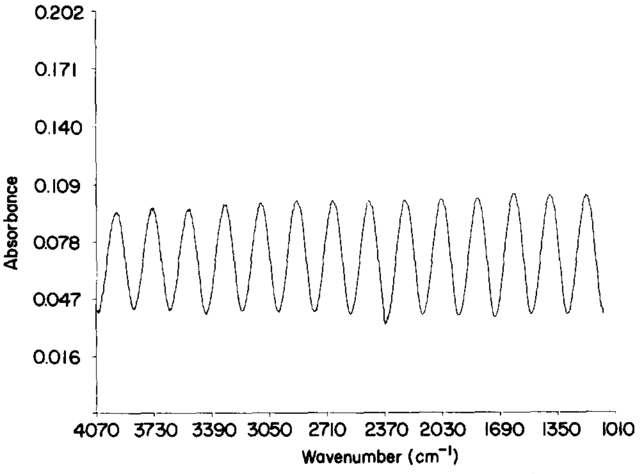

Figure 4 Interference fringes arising from multiple reflections between the internal surfaces of the cell windows

where C_0 is initial concentration of the absorbing species. In order to verify the data obtained by the *FT*i.r. technique, the disappearance of the isocyanate group was also followed by the classical titration with n-butylamine. The plot of *P versus* time in *Figure 5* shows a fair agreement between the results obtained from both methods[11]. Note that whereas titration cannot be used beyond the onset of gelation, the reaction may be followed by i.r. absorption until complete conversion. On the other hand, the chemical titration of double bonds is not possible for the acrylic component, due to the presence of the PUR network, so that only *FT*i.r. allows one to follow the formation of PAc.

Comparison of the laboratory synthesis and the in-cell synthesis

A 34/66 PUR/PAc IPN was synthesized as a thin film (16 μm), following the experimental conditions described earlier. Its spectra was compared with that obtained from a film (20 μm) directly synthesized in the i.r. cell. The absorption behaviour of both films is identical.

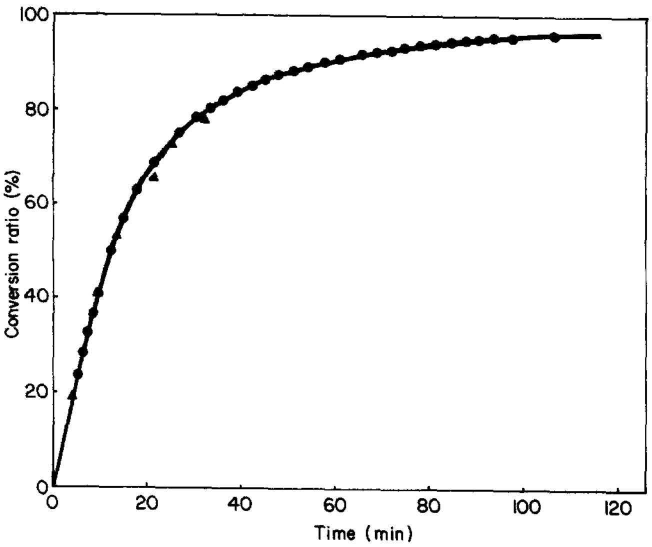

Figure 5 Conversion ratio of NCO as a function of time, by *FT*i.r. (●) and chemical titration (▲)

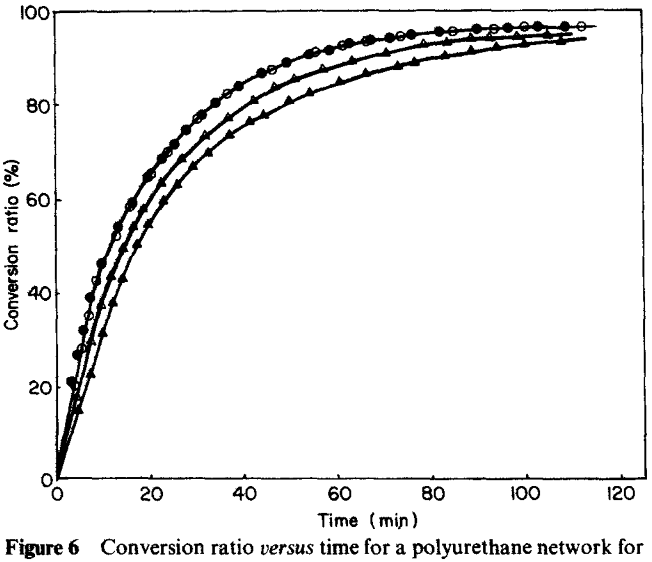

Figure 6 Conversion ratio *versus* time for a polyurethane network for various catalyst concentrations: 0.38% (▲); 0.50% (△); 1.0% (○); 2.0% (●). PUR concentration in ethyl acetate is 25 wt%

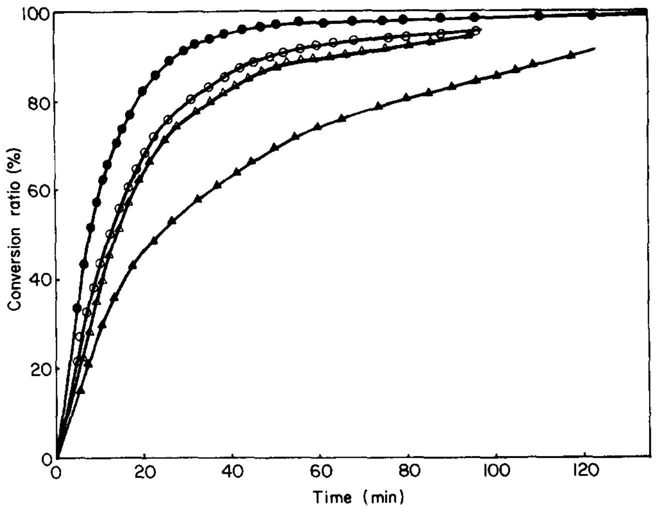

Figure 7 Conversion ratio *versus* time for the polyurethane network for various solvent concentrations: 10/90 (▲); 25/75 (△); 50/50 (○); 70/30 (●). Catalyst concentration is 1.05%

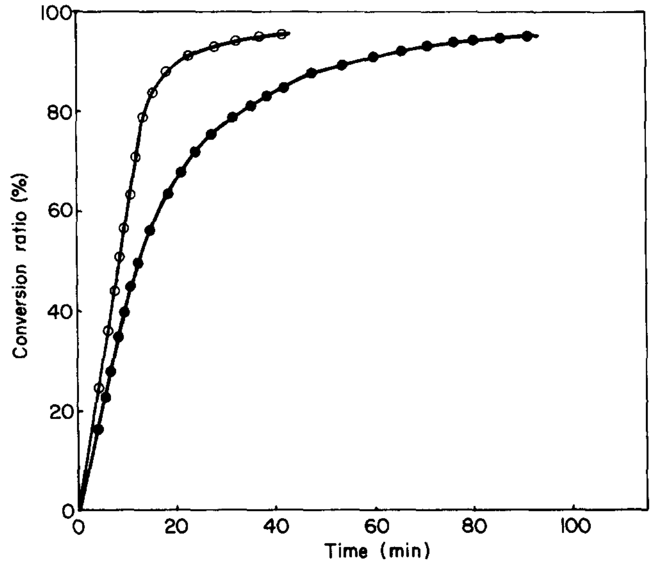

Figure 8 Conversion ratio *versus* time for a polyurethane network at different temperatures: 25°C (●), 43°C (○). PUR concentration in ethylacetate is 25 wt%, OcSn concentration is 1.05%

Preliminary kinetic studies of the individual networks and of an IPN

Having established the validity and the limits of the determination of conversion ratios by absorbance measurements, we have applied the method to the individual PUR and PAc networks, as well as to a 34/66 IPN.

PUR network. The acrylic monomer has been replaced by a solvent, ethyl acetate, in order to avoid any accidental polymerization. The parameters affecting the kinetics of PUR network formation are: the catalyst concentration, the concentration of isocyanate (and diol) in the reaction medium, and the temperature. *Figures 6* to *8* show the main results: for a 25/75 PUR precursor concentration in ethyl acetate, the time to reach gelation, t_{gel}, decreases with increasing percentage content of OcSn, but it seems that above a critical concentration of about 1%, the effect becomes less pronounced. Djomo *et al.*[12] have observed the same behaviour. If now the percentage of OcSn is kept constant (1.05%, i.e. above the critical concentration), and

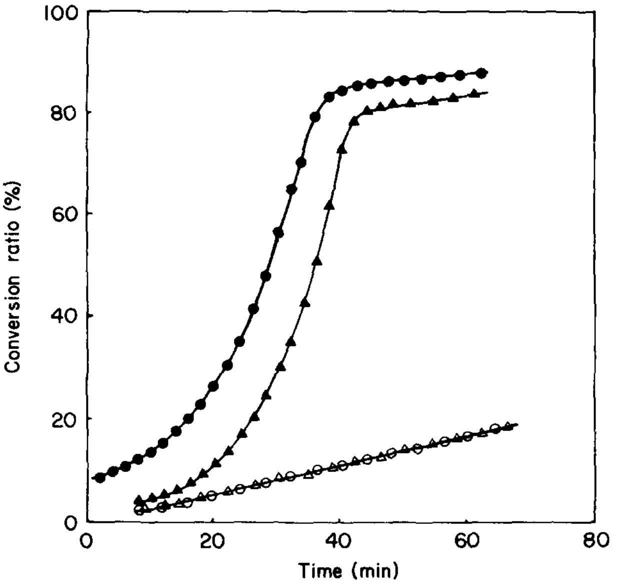

Figure 9 Conversion ratio *versus* time for poly(methyl methacrylate): without TRIM (○); without TRIM and with OcSn (1.45%) (△); with Trim (5%) (▲); with OcSn (1.45%) and TRIM (5%) (●)

the concentration of isocyanate in the solvent increases, t_{gel} decreases, probably due to the higher probability of encounter between the reagents. Finally, the formation of PUR also becomes faster when the temperature of the reaction medium is raised.

Polyacrylic network. Some results of the radical copolymerization of the acrylic system appear in *Figure 9*. The effect of the crosslinker (TRIM) is to speed up the reaction: the acceleration is very important as compared to the formation of the linear PMMA. The presence of OcSn also has an accelerating effect on the copolymerization, which has already been reported[13]. It takes place in the initial step, whereas the slopes of the curves during the propagation step remain parallel.

34/66 PUR/PAc IPN. An IPN containing 34% PUR was prepared and its synthesis followed by *FT*i.r. spectroscopy (*Figure 10*). The conversion *versus* time curves were recorded simultaneously. An immediate observation is that both curves are identical to those obtained separately; there is no mutual interference between the two systems.

CONCLUSION

The validity of *FT*i.r. spectroscopy for the study of the synthesis of IPNs has been established. In a following paper, the results obtained on the individual networks and the IPN will be developed and interpreted quantitatively.

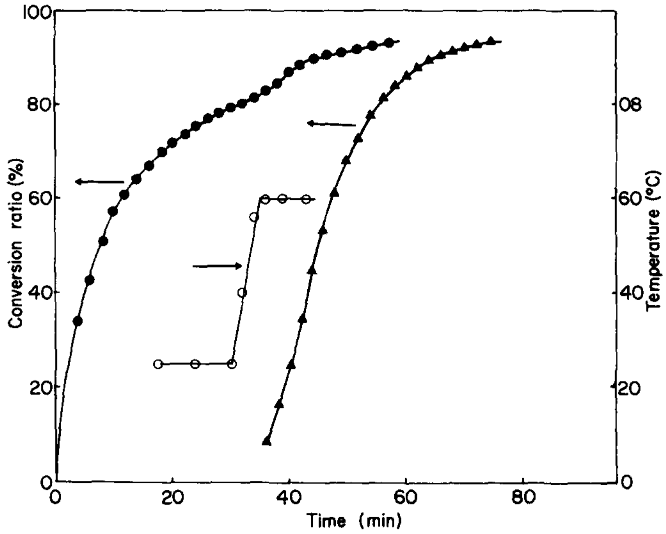

Figure 10 Conversion ratio *versus* time for an IPN (34/66): PUR (●); PAc (▲); temperature cycle (○)

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