

# Investigations for Obtaining Semi-Interpenetrating Polymer Networks Based on Monomers of Different Reactivity Toward Radicals

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## SYNOPSIS

Classically, the one-step synthesis of interpenetrating polymer networks (IPNs) and related materials requires noninterfering polymerization modes to achieve distinct networks, held together by only physical entanglements. For the combination of (meth) acrylic and allylic monomers, both polymerizable by free radicals, a new *in situ* sequential synthesis for obtaining semi-IPNs is proposed. Using specific initiators that decompose at two different temperatures, refractive index measurements, Fourier transform infrared spectroscopy, and dynamic mechanical analysis have shown that neat species are formed and that the two monomers do not copolymerize. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer blending is a useful technique to obtain properties not readily achieved in homopolymers. Interpenetrating polymer networks (IPNs) are a special type of polymer blends<sup>1-3</sup> in which the polymers coexist in the form of their physically entangled networks. These materials exhibit interesting characteristics compared with other combinations including block or graft copolymers and are the only way in which cross-linked polymers may be intimately combined. Hence, formation of IPNs requires specific ways of mixing due to the cross-linked nature of the components. Two major techniques are described in the literature as successful for the preparation of IPNs: The first one is a sequential process<sup>4-6</sup> in which a preformed network is swollen with the reactants (monomer, cross-linker, initiator) necessary to form the second network, after which the monomer is polymerized inside the primary network. The use of the sequential polymerization method enables IPNs to be prepared according to the same mechanism, i.e., free-radical polymerization, without danger of forming internetwork bonds.

It is also possible to use the same monomer to build both networks.<sup>7</sup>

The simultaneous process,<sup>8,9</sup> better named *in situ* synthesis,<sup>10-12</sup> involves mixing of monomers or low molecular weight prepolymers with their respective cross-linkers and initiators or catalysts, and forming more or less simultaneously the two networks via noninterfering reaction mechanisms. Hence, the choice of the monomers forming each network is limited to those components that are mutually miscible in the early stage of the process and that do not react with each other under the polymerization conditions. For example, a system that has received much attention is that based on polyurethanes, formed by a step-growth mechanism, and (meth) acrylic polymers, formed by a chain-growth mechanism.<sup>13-17</sup> Polyurethanes are widely used in polymer industries, and IPNs based on polyurethane and poly(methyl methacrylate) are very attractive materials. However, for some particular applications, like in optics, CR 39 resins or similar diallylic polymers are preferred to poly(methyl methacrylate). If one simply exchanges the monomers, i.e., replaces the methacrylate by a diallylic monomer, IPNs can no longer be made by the *in situ* process since the initial mixture of the constituents is inhomogeneous due to the precipitation of isocyanate in the allylic monomer. Consequently, polyurethane

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cannot be associated with such monomers and has to be replaced by another elastomer.

Poly(butyl acrylate), which is rubbery at room temperature, may be used similarly to polyurethane. In that case, the initial mixture is clear and homogeneous as the monomers are mutually miscible, but the difference in the polymerization mechanism that is required for IPN formation is no more fulfilled as both monomers polymerize under free-radical conditions. However, one should be able to obtain such IPNs because these monomers have quite different reactivities toward free radicals: The allylic C=C double bonds are about 100 times less reactive than are vinyl or (meth)acrylic double bonds.<sup>18</sup> Also, cross-linking of a diallylic monomer takes place at the end of polymerization and requires a temperature higher than that of a (meth)acrylic polymerization.<sup>19,20</sup>

In this study, experimental investigations were made to elaborate an entirely radical process of obtaining *in situ* IPNs based on butyl acrylate (BuA) or butyl methacrylate (BuMA) and diallyl carbonate of bisphenol A (DACBA). A sequential procedure was suggested considering polymerization and cross-linking of the most reactive monomer first, and only this one, followed by the formation of the diallylic network after completion of the first polymerization. The formation of the two networks was studied by refractive index measurements and infrared spectroscopy. The material thus obtained was characterized by its dynamic mechanical behavior.

## EXPERIMENTAL

The monomers, butyl acrylate (BuA, Aldrich), butyl methacrylate (BuMA, Merck), and diallyl carbonate of bisphenol A (DACBA, Pittsburgh Plate Glass Co.), were dried over molecular sieves, but not otherwise purified. The initiators, azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), and *t*-butyl peroxy isononanoate (TBPIN), were used as received. The initial mixture was prepared by weighing the required amounts of BuA or BuMA, DACBA, and the free-radical initiator, stirring thoroughly in a dry nitrogen atmosphere and pouring into a glass mold, giving 3 mm-thick plates. When using BuA, 1% by volume of dodecanethiol (Merck) was added as a chain transfer agent. BPO or TBPIN were added in the amount of 3% by weight, whereas the amount of AIBN was only 1% to avoid trapped nitrogen in the sample. The weight ratio of the (meth)acrylic monomer to the allylic monomer was 1 : 1 in the reaction mixture. The mold was heated

in a water bath at temperatures ranging from 50 to 80°C for various periods of time. An oven was used for higher temperatures.

The refractive index,  $n$ , of the reaction mixture was determined at 21°C using a thermostated OPL refractometer. The consumption of the C=C double bonds was followed by Fourier transform infrared (FTIR) spectroscopy on a Nicolet 60SX apparatus equipped with a heating chamber. For FTIR experiments, the mixture was injected in a cell formed by two NaCl windows separated by a 20  $\mu$ m-thick gasket. Dynamic mechanical measurements were performed with a Rheometrics RMS 7200 mechanical spectrometer at a fixed frequency of 1 rad/s through a temperature range from -100 to 150°C under dry nitrogen. The applied strain was 1%.

## RESULTS AND DISCUSSION

Tentatives to elaborate an entirely radical *in situ* process were first made in the absence of a cross-linker. DACBA as a difunctional monomer leads directly to a tridimensional structure, and formation of semi-2 IPNs<sup>1</sup> is expected. Similarly, full IPNs may be obtained just by introducing a suitable cross-linker. Preliminary attempts were made by using BPO as free-radical initiator: For pure DACBA in bulk, no noticeable increase in viscosity could be noted after 24 h heating at 50°C, but at 60°C, a change in viscosity was observed after 4 h; at 70°C, the reaction medium was solid after 1 h. From these experiments, by fixing reaction temperature at 60°C, one expects the (meth)acrylic monomer to polymerize to completion (this occurs usually within 1 h<sup>10</sup>) before the onset of polymerization of DACBA.

Because of the noticeable difference in refractive indexes between monomers as well as between polymers (see Table I), it is possible to follow the polymerization of each monomer from the value of the refractive index of the reaction medium. The variation of the refractive index with time for a 50/50

**Table I** Refractive Index

Material	Refractive Index (21°C)	
	Monomer	Polymer
BuA	1.417	1.466
BuMA	1.423	1.483
DACBA	1.537	1.566

Accuracy:  $\pm 0.001$ .

BuA/DACBA mixture, heated at 60°C in the presence of BPO, is displayed in Figure 1. At the beginning, the experimental refractive index corresponds to the mixture of the monomers. If only BuA were to have been polymerized, one would have reached a limiting value that corresponds to that of a 50/50 mixture of poly (butyl acrylate) and DACBA monomer. In fact, higher values were found and the curve continued to increase, indicating the participation of DACBA. Hence, one must conclude that both monomers copolymerize randomly, despite their difference in reactivity, with a gradual enrichment in DACBA, and the result is not an IPN, but, rather, an AB cross-linked polymer.

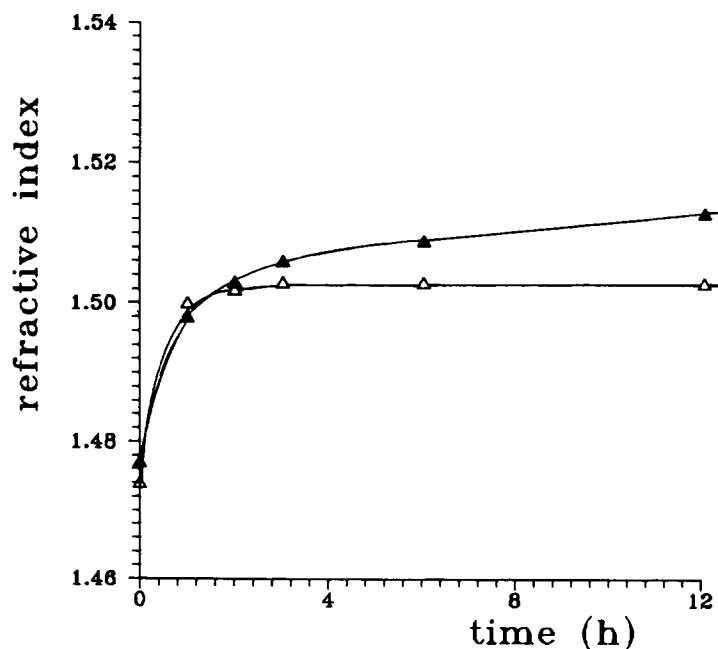
As a consequence, the idea was to replace BPO by two free-radical initiators, each specific to one monomer. This requires a sequential initiation of the monomers, which may be done by operating at two different temperatures, with adequate initiators that decompose at these temperatures.

Obviously, the (meth) acrylic monomer, which is the most reactive, has to be polymerized first, using AIBN, a classical free-radical initiator for this monomer that does not initiate the polymerization of allylic monomers when amounts lower than 1% by weight are used. Appropriate temperature for decomposition is 60°C. On the other hand, to avoid an untimely initiation of DACBA, TBPIN, a peroxidic initiator that decomposes into radicals only

above 90°C, was selected in association with AIBN. Consequently, the *in situ* sequential process consists in a first period of heating at 60°C, followed by another period at 95°C.

The selectivity of AIBN and TBPIN toward BuA and DACBA, respectively, was checked through refractive index measurements. In the presence of 1 wt % AIBN, the refractive index of DACBA remains constant at  $n = 1.537$ , even after heating 7 h at 60°C. On the other hand, when BuA is mixed with 3 wt % TBPIN, no change in refractive index is observed after the same conditions of time and temperature. Finally, the variation of the refractive index with time of a 50/50 BuA/DACBA mixture containing AIBN and TBPIN (see Fig. 1) indicates that at 60°C only BuA polymerizes without the participation of DACBA, as a plateau is reached. Also,  $n$  remains constant as long as the temperature is maintained at 60°C.

The complete process, i.e., the polymerization of a mixture of BuA or BuMA and DACBA containing AIBN and TBPIN was examined by Fourier transform infrared (FTIR) spectroscopy, and reaction conversion was calculated from the change of the normalized absorbance of the C=C bond stretching mode in the 1630–1650  $\text{cm}^{-1}$  region: The spectra display a strong peak at 1639  $\text{cm}^{-1}$ , characteristic of (meth) acrylic functions, with a shoulder at 1649  $\text{cm}^{-1}$ , which corresponds to the allylic monomer.



**Figure 1** Refractive index vs. time curves of a 50/50 BuA/DACBA mixture in presence of (▲) BPO or (△) AIBN + TBPIN. Reaction temperature: 60°C.

When temperature is maintained at 60°C, the intensity of the 1639  $\text{cm}^{-1}$  peak decreases and reaches the base line. Meanwhile, the shoulder emerges from the main peak to give a single peak, the intensity of which does not change until the reaction medium is heated up to a temperature of 95°C. Then, it decreases slowly with time, revealing that DACBA polymerizes.

The overall consumption of the C=C double bond during polymerization is shown in Figures 2 and 3 for a 50/50 BuA/DACBA mixture and a BuMA/DACBA mixture, respectively. During the first 3 h, temperature was set at 60°C, then increased to 95°C.

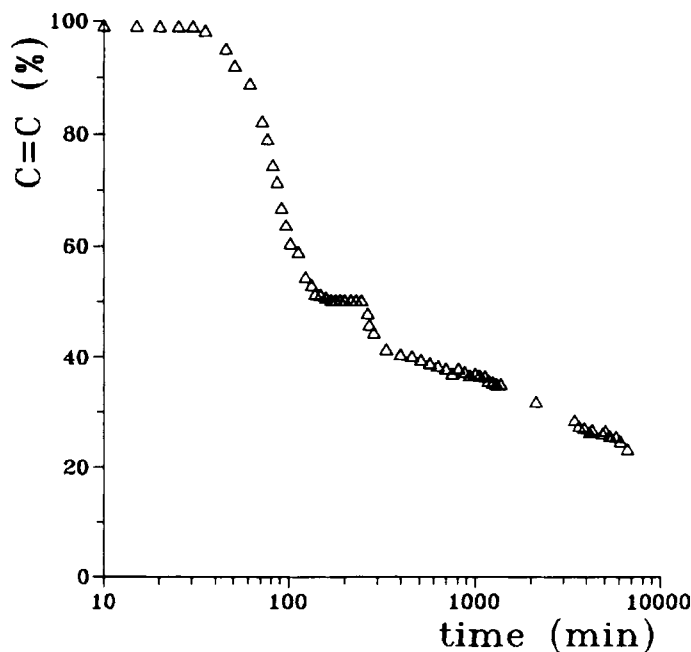
For both systems, an intermediate plateau is reached, corresponding to 96% conversion of butyl (meth)acrylate. The main difference between the curves concerns the rate of polymerization: As expected, BuA polymerizes more rapidly than does BuMA, though after a longer initiation period. The second part of the kinetic profile is similar in shape to the conversion curve of DACBA in bulk. The end-conversion for this step depends on the nature of the polymer already formed: 52% and 46% for DACBA in the presence of poly(butyl methacrylate) and poly(butyl acrylate), respectively, compared to 65% for DACBA in bulk. Because at this stage the free-radical polymerization is diffusion-controlled,

chain transfer to the monomer, which is the prevailing termination mechanism, is more likely to occur as the viscosity of the medium is higher due to the presence of poly(meth)acrylate. However, the difference between both systems is not yet explained.

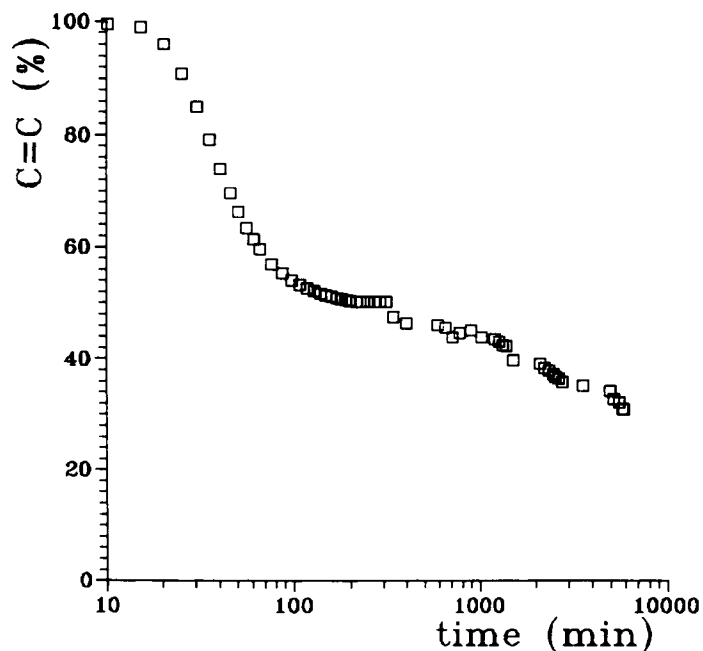
The possible action of propagating (meth)acrylic radicals toward DACBA also has to be considered: Such a reaction would actually introduce allyl mers into the elastomeric polymer. To examine this point, before increasing temperature, the reaction medium was diluted with ethyl acetate and the polymer (which was still soluble) precipitated in hexane. UV analysis of the polymer did not show the presence of aromatic rings coming from DACBA. Hence, one can exclude participation of the allylic monomer in the polymerization of BuA or BuMA, at least within experimental error.

The FTIR experiments, confirmed by refractive index measurements, and the UV results indicate that, in a first approach, two separate polymers are formed, both by a free-radical mechanism. Consequently, a two-phase material should have been obtained, as (meth)acrylic and allylic polymers are incompatible.

The phase behavior can be reflected, at least qualitatively, by the dynamic mechanical behavior of the material. The temperature dependence of the dissipation factor,  $\tan \delta$ , for the 50/50 BuMA/



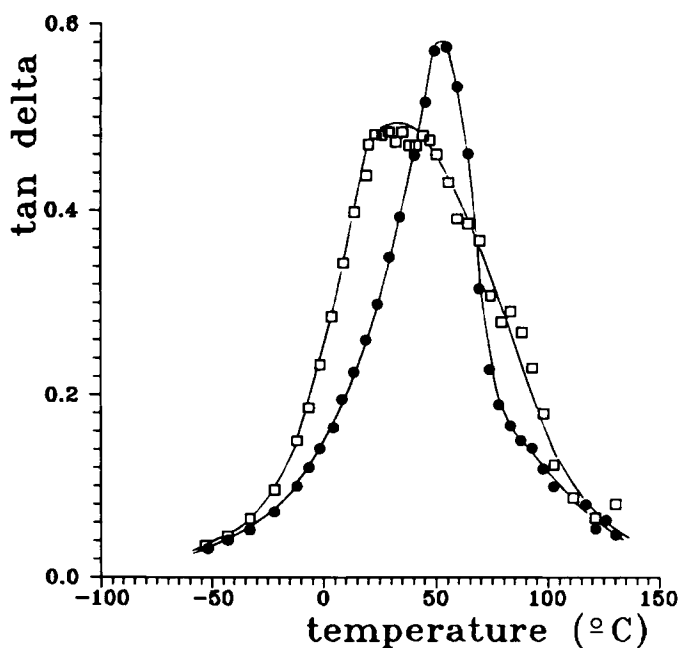
**Figure 2** Overall consumption of C=C bonds during polymerization of a 50/50 BuA/DACBA mixture with AIBN and TBPIN as free-radical initiators. Synthesis temperatures: 60°C during the first 180 min, then 95°C.



**Figure 3** Overall consumption of C=C bonds during polymerization of a 50/50 BuMA/DACBA mixture with AIBN and TBPIN as free-radical initiators. Synthesis temperatures: 60°C during the first 180 min, then 95°C.

DACBA system is shown Figure 4. The behavior of the end material obtained with two initiators, AIBN and TBPIN, at two levels of temperature, 60 and 95°C, is compared to that of the corresponding cross-

linked copolymer obtained by heating the monomer mixture directly at 95°C, with only TBPIN, for a simultaneous onset of both polymerizations. In the latter case, one observes a narrow peak located be-



**Figure 4** Loss tangent vs. temperature curves of polymerized 50/50 BuMA/DACBA mixtures. Free-radical initiators: (●) TBPIN (95°C); (□) AIBN (60°C) + TBPIN (95°C).

tween the two glass transition temperatures of the homopolymers, as classically found for random copolymers. On the other hand, the end material issued from the sequential process developed here exhibits a damped and broad transition, typically what is observed for interpenetrating polymer networks, in which gross phase separation is impeded due to their peculiar synthesis mode.

## CONCLUSION

These results indicate that two individual phases are formed by the use of specific free-radical initiators, viz., AIBN at 60°C and TBPIN at 95°C. One point that remains to be clarified is the probability of interphase grafting that may occur by transfer of the allylic propagating radicals to the already-formed (meth) acrylic polymer. In fact, this may also occur in sequential or in classical simultaneous synthesis methods involving allylic monomers. Using electron spin resonance spectroscopy, preliminary results indicating no grafting have been reported elsewhere.<sup>21</sup> Hence, one can assume the formation of a semi-interpenetrating polymer network based on poly(butyl acrylate) or poly(butyl methacrylate) and a diallylic network by an entirely free-radical mechanism.

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Received April 10, 1992

Accepted July 15, 1992