Interference between Reactants in Simultaneous Interpenetrating Polymer Network Formation. 1. Influence of Tin Catalyst on Free-Radical Copolymerization of Methyl Methacrylate with Trimethylolpropane Trimethacrylate

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ABSTRACT: Simultaneous interpenetrating polymer networks (IPNs) based on polyether polyurethane (PUR) and poly(methyl methacrylate-*co*-trimethylolpropane trimethacrylate) (PMMA) were prepared in bulk at 60 °C. The gelation time of the individual PMMA network was found to be faster when using azobis(isobutyronitrile) (AIBN) in the presence of stannous octoate ($SnOc_2$) as activating system, compared to pure AIBN. Kinetic measurements have shown that the synergistic $SnOc_2$ role concerns the initiation of the free-radical polymerization. The results were explained by assuming the formation of a cyclic complex between the nitrile groups of AIBN and the tin(II) atom of $SnOc_2$.

Introduction

Interpenetrating polymer networks (IPNs) are combinations of two or more cross-linked polymers held together by permanent entanglements, obtained under special preparation methods.[1−3] One process industrially suitable is by a one-step (in situ) polymerization in which all monomers or prepolymers are first mixed together before polymerization/cross-linking of either component. Such synthesis requires noninterfering routes for the two polymerizations, typically a step-growth mechanism and a chain polymerization. Therefore, the IPNs synthesized to date are often based on polyurethanes and conventional vinyl polymers, polystyrene or poly(methyl methacrylate).[4−9]

Generally, most IPNs exhibit a limited phase-separated structure, compared to other types of blend. Among the parameters that control the extent to which IPNs undergo phase separation, the relative reaction rates of network formation play a predominant role.[10,11] Studies on kinetic effects involved in IPN formation in relation with their morphology and properties have been the subject of a recent review.[12] In previous publications on simultaneous polyurethane/poly(methyl methacrylate) (PUR/PMMA) IPNs, we have reported that a key variable to obtain a large spectrum of physicochemical properties at a given composition was the relative rate of the formation reactions.[13−15] Control of the reaction conditions was achieved simply by changing temperature, choice, and amount of catalyst and/or free-radical initiator. For instance, when the concentration of catalyst is decreased, the formation of the polyurethane network becomes slower, as expected, but the kinetics of formation of the PMMA network is also modified. The explanation for this unexpected effect, not seen in case of in situ sequential synthesis,[16] should be found by considering either the presence in the medium of the precursors of the PUR network, still reactive compounds (isocyanate, alcohol, catalyst), or the rheological change, typically increase of viscosity, of the medium, due to the step-growth reaction which proceeds simultaneously.

There are very few kinetic studies related to free-radical cross-linking copolymerization of MMA with low concentration of multifunctional vinyl monomers.[16−19] However, it has been shown that an increase in the concentration of cross-linker induces higher polymerization rates[16,17,20] and autoacceleration (Trommsdorff effect) at lower conversion ratios.[16,17] Also, termination rate decreases significantly and reduces end conversion to lower values, due to trapped inactive radicals[21] and higher glass transition temperature (T_g), for cross-linked PMMA compared to linear PMMA.[17,22,23] The presence of a solvent leads to the same results, namely delay and reduction of the Trommsdorff effect and increase of the end-conversion ratio, for linear and for cross-linked PMMA.[17,19] The mechanism generally admitted[19,24] consists of the formation of microgels at the early stage of the cross-linking copolymerization. As the reaction proceeds, the concentration of these microgels increases up to agglomeration and gelation of the reactive medium.

The gel point can be defined as the transition between a viscous solution and a viscoelastic medium.[25] Rosenberg and Flodin[26] have studied the cross-linking copolymerization of MMA with trimethylolpropane trimethacrylate (TRIM) and the homopolymerization of TRIM by nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC). They have defined the gel point as the change of the slope of the conversion versus time curves at low conversion. Several authors[20,27] have shown that the increase of concentration of the cross-linking agent does not change the gel point. However, dilution of the reactive media highly increases the conversion at the gel point quasi-linearly.[27,28] Sev-

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eral theories for cross-linking copolymerization have been proposed. They can be classified as percolation,[29] statistical,[30,31] and kinetic[18,32,33] models.

As a part of a continuing study of the kinetics of formation of IPNs, the objective of the present study was to clarify the role of stannous octoate ($SnOc_2$), which is the catalyst used for the formation of polyurethane, on the kinetics of PMMA formation, since organometallic compounds are known to influence the polymerization rate of vinyl and acrylic monomers.[34-37] In this work, we report on the kinetics of free-radical polymerization of MMA and cross-linking copolymerization of MMA with TRIM, thermally initiated by the decomposition of AIBN, under various conditions: in bulk, in the presence of an inert solvent, and in the presence of a reactive solvent, i.e., the precursors of the PUR network, typically under the conditions leading to in situ simultaneous IPNs. The influence of various organotin compounds was examined.

Experimental Section

Materials. The monomers were dried over 4 Å molecular sieves but not otherwise purified. Methyl methacrylate (MMA) (Merck) contained 100 ppm hydroquinone and 75 ppm water. 1,1,1-Trimethylolpropane trimethacrylate (TRIM) (Degussa), used as cross-linker at a level of 5 wt %, contained 100 ppm hydroquinone monomethyl ether and 250 ppm water. The initiator of the free-radical polymerization, 2,2-azobis(isobutyronitrile) (AIBN) (Merck), was recrystallized from methanol before use. The tin compounds were used as received. Very sensitive to oxygen, stannous octoate ($SnOc_2$) (K29, Goldschmidt) was stored under nitrogen at low temperature. Tin content: 29.3 wt %. Dibutyltin dilaurate (DBTDL) (K19, Goldschmidt) contained 18.5 wt % tin. Dibutyltin bis(2-ethylhexanoate) (DBTEH) (Alfa Johnson Matthey), 22.9 wt % tin, was used in powdery form. The solvent ethyl acetate (Merck, 99.5% purity) was dried over 4 Å molecular sieves before use.

Synthesis. Formation of PMMA networks by free-radical copolymerization of MMA and TRIM has been widely described in the case of in situ sequential and simultaneous PUR/PMMA IPNs.[13,14,16] The preparative method for individual PMMA networks was identical, except that the polyurethane precursors, i.e., 1.07 equiv of aromatic polymeric isocyanate and 1.0 equiv of polyoxypropylene glycol of molecular weight (MW) 2000, were replaced by the solvent. Reactions were conducted in nitrogen-purged Pyrex tubes at 60 °C in a water bath. The immersion of the tubes was taken as the origin of time. A series of five PUR/PMMA IPNs of various compositions—0/100, 15/85, 25/75, 34/66, and 50/50—were prepared.

Characterization. A Nicolet 60SX Fourier transform infrared (FTIR) spectrometer equipped with a Specac heating chamber was used to follow the reaction kinetics. The reaction mixture was injected in a cell formed by two NaCl windows separated by a 25 μm thick gasket. The spectra were recorded at 2 cm^{-1} resolution, and 32 consecutive scans were collected for signal averaging. Reaction conversion was calculated from the change of the normalized absorbance of the C=C stretching vibration at 1639 cm^{-1}, making sure of the validity of the Beer–Lambert law. This peak, not overlapping with its neighbors, showed a gradual decrease as the copolymerization of MMA with TRIM proceeds. To compensate the volume contraction during copolymerization, the C–H peak at 2870 cm^{-1} was chosen as internal standard.

Gel points were determined visually as being the conversion at which the reaction medium would no longer flow, i.e., when a small needle would no longer penetrate the reaction medium.

Results and Discussion

The kinetics of copolymerization of MMA with TRIM during the formation of in situ simultaneous PUR/PMMA IPNs are presented in Figures 1 and 2 for two compositions, 25/75 and 50/50, respectively, using various amounts of stannous octoate ($SnOc_2$), the catalyst of the isocyanate/alcohol reaction. Despite constant reaction temperature (60 °C) and constant amounts of cross-linker (5 wt %) and of free-radical initiator (AIBN, 1 wt %), the C=C conversion versus time curves are not superimposable, indicating that the simultaneous formation of the polyurethane network kinetically interfered with the formation of the methacrylic network. Three effects can be seen: (i) The initiation period is reduced with increasing concentration of $SnOc_2$; however, propagation rates are identical since the slope of the various curves is the same between 20% and 80% conversion. (ii) The Trommsdorff effect appeared earlier when increasing the concentration of $SnOc_2$. (iii) Contrary to the bulk polymerization of MMA, a final conversion of 100% is reached in every case.

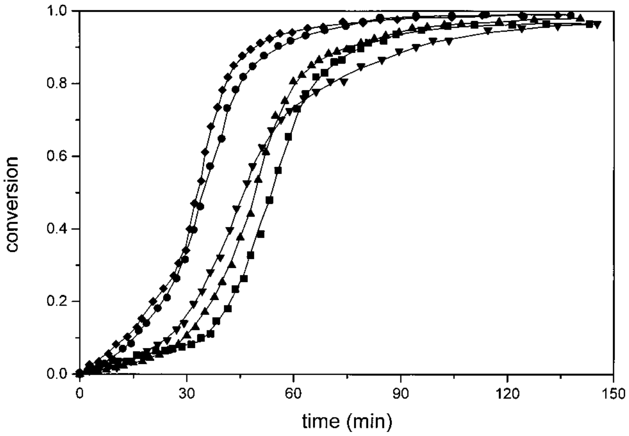


Figure 1. C=C conversion versus reaction time for the copolymerization of MMA with TRIM during synthesis of 25/75 in situ simultaneous PUR/PMMA IPNs at 60 °C. Formation of PUR network was catalyzed by various amounts of $SnOc_2$: (■) 0.1 wt %; (▲) 0.2 wt %; (▼) 0.35 wt %; (●) 0.5 wt %; (◆) 1.0 wt %.

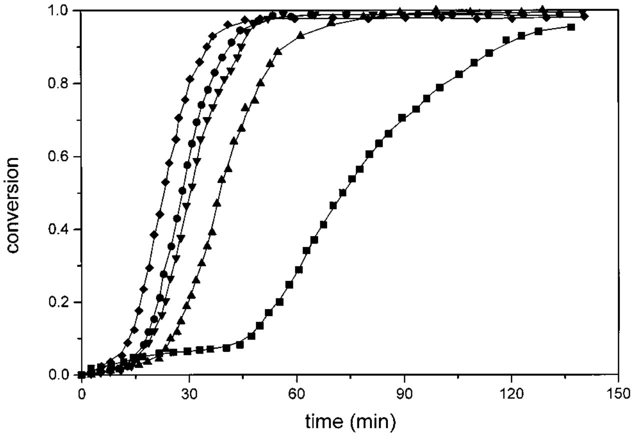


Figure 2. C=C conversion versus reaction time for the copolymerization of MMA with TRIM during synthesis of 50/50 in situ simultaneous PUR/PMMA IPNs at 60 °C. Formation of PUR network was catalyzed by various amounts of $SnOc_2$: (■) 0.1 wt %; (▲) 0.2 wt %; (▼) 0.35 wt %; (●) 0.5 wt %; (◆) 1.0 wt %.

The latter effect, previously seen for in situ sequential PUR/PMMA IPNs,[16] can be explained by the dilution of the reaction medium and by its glass transition temperature, which is lower than the temperature of synthesis. Explanation of the two other effects may be as follows: viscosity change of the medium and influ-

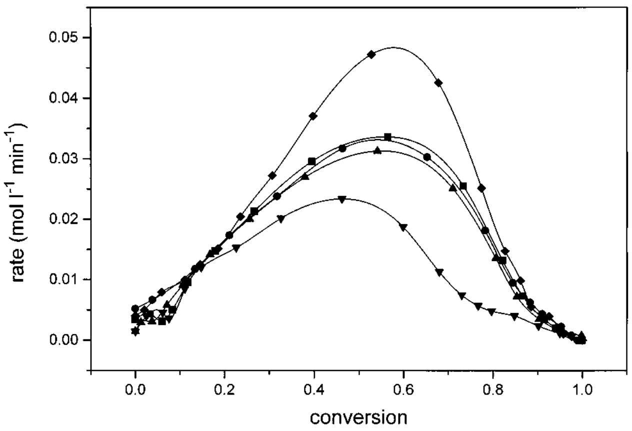


Figure 3. MMA/TRIM copolymerization rates during synthesis of 25/75 in situ simultaneous PUR/PMMA IPNs at 60 °C. Presence of SnOc$_2$ in the reaction medium: (■) 0.1 wt %; (▼) 0.35 wt %; (●) 0.5 wt %; (◆) 1.0 wt %.

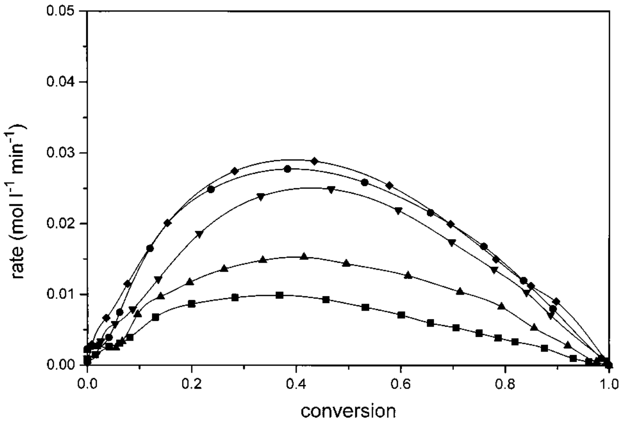


Figure 4. MMA/TRIM copolymerization rates during synthesis of 50/50 in situ simultaneous PUR/PMMA IPNs at 60 °C. Presence of SnOc$_2$ in the reaction medium: (■) 0.1 wt %; (▲) 0.2 wt %; (▼) 0.35 wt %; (●) 0.5 wt %; (◆) 1.0 wt %.

ence of SnOc$_2$ on initiation of free-radical polymerization. At a given time, it is evident that an increase of the catalyst concentration leads to a faster formation of the PUR network and, therefore, to an increase of the viscosity of the reactive medium. The consequence is a decrease of the initiation period of the free-radical polymerization and an earlier appearance of the Trommsdorff effect. The fact that the system cross-links should also be taken into account. However, conversion of MMA at the gel point cannot be calculated either theoretically or experimentally since gelation highly depends on synthesis conditions.[27,28] According to Rosenberg and Flodin,[26] gelation occurs when the slope of the kinetic curves changes suddenly; this corresponds in our case to a conversion range of 5−11%, which is also the beginning of the Trommsdorff effect.

The variation of the copolymerization rate of the methacrylic components versus conversion of C=C double bonds is shown in Figures 3 and 4 for the two compositions studied. It can be seen that the rate increases significantly from about 10% conversion; however, the change of the rate profile with the concentration of the polyurethane catalyst is difficult to explain. Only the methacrylic system formed in the 50/50 IPN (Figure 4) exhibits a regular variation of the curves with the concentration of SnOc$_2$. For the 25/75 IPN, the profile of the curves may result from the intense acceleration of the kinetics due to the Trommsdorff effect, associated with the calculation method (derivation), or from the simultaneous formation of PUR and concomitant viscosity increase of the medium.

This explanation of the initial increase of the formation rate of the PMMA network is satisfactory, but incomplete, in our case. Replacement of the simultaneously developing polyurethane system by an inert solvent would be useful to suppress the influence of viscosity and to determine better the role of SnOc$_2$. Therefore, only the formation of PMMA networks in bulk or in solution is considered hereafter.

Table 1 gives the results of copolymerization tentatives of MMA and TRIM in the presence of AIBN and SnOc$_2$ at two temperatures, 25 and 60 °C, respectively. Experiments were conducted in the dark to prevent accidental photopolymerization. As expected, in the absence of AIBN or SnOc$_2$, no polymerization occurs. Also, at room temperature, neither AIBN nor SnOc$_2$ alone initiates the chain copolymerization. Only the couple AIBN/SnOc$_2$ leads to a network, in about 3 or 24 h when operating in bulk or in solution, respectively. At 60 °C, SnOc$_2$ is still inactive toward the methacrylic monomers, but combined with AIBN, gelation occurs twice as fast than with only AIBN, thus confirming the synergistic effect of the couple AIBN/SnOc$_2$ on the kinetics of free-radical copolymerization of MMA and TRIM in simultaneous IPNs.

Under the same experimental conditions, replacement of SnOc$_2$ by organotin(IV) compounds such as dibutyltin dilaurate (DBTDL) or dibutyltin bis(2-ethylhexanoate) (DBTEH) does not allow the formation of a methacrylic network when associated with AIBN at room temperature (see Table 2). At 60 °C, gelation occurs but significantly more slowly than when using pure AIBN. Hence, contrary to the couple AIBN/SnOc$_2$, combinations of AIBN with tetravalent organotin compounds have no synergistic effects on the free-radical polymerization of MMA, thus confirming the particular role played by SnOc$_2$ due to its bivalent tin.

The copolymerization kinetics of MMA with TRIM were determined in bulk and in solution at 60 °C using FTIR, and conversion profiles are shown in Figure 5 for various concentrations of SnOc$_2$, but with fixed values of AIBN and TRIM. In ethyl acetate, the formation of the methacrylic network is accelerated by the presence of SnOc$_2$. Further, it is dependent on the amount of organotin compound. The effect of SnOc$_2$ seems to concern the rate of initiation of the copolymerization since at the beginning of the reaction (up to 40 min) the conversion of the C=C double bonds is more important in the presence of SnOc$_2$. However, propagation rate and termination rate seem to be unaffected by SnOc$_2$ (identical slope for all curves).

Copolymerization with TRIM and homopolymerization of MMA were also performed in polyoxypropylene glycol as solvent and in bulk. As previously, 1 wt % AIBN was used. These curves (Figure 5) again show that SnOc$_2$ (1 wt %) influences the initiation rate of the chain reaction, independently of the nature and concentration of the solvent and of the presence or absence of cross-linker. In the case of homopolymerization of MMA in bulk, 10% conversion is reached in about 1 h without SnOc$_2$ when only 40 min is sufficient in the presence of SnOc$_2$.

Some authors have reported an increase of the polymerization rate of vinyl and acrylic monomers in the presence of organometallic compounds. The explanation

Table 1. Gelation of the Methacrylic Monomers under Various Conditions

		MMA-*co*-TRIM			
		in bulk[a]		in 34% ethyl acetate[b]	
[AIBN] (wt %)	[SnOc$_2$] (wt %)	60 °C	25 °C	60 °C	25 °C
0	0	no gel	no gel	no gel	no gel
0	1	no gel	no gel	no gel	no gel
1	0	gel in 20 min	no gel	gel in 32 min	no gel
1	1	gel in 8 min	gel in 180 min	gel in 15 min	gel in 24 h

[a] Yield after 15 h of reaction. [b] Yield after 60 h of reaction.

Table 2. Effect of the Presence of Organotin(IV) Compounds on Gelation of the Methacrylic Monomers in Bulk

[AIBN] (wt %)	[DBTDL] (wt %)	[DBTEH] (wt %)	MMA-*co*-TRIM in bulk[a]	
			60 °C	25 °C
0	1	0	no gel	no gel
0	0	1	no gel	no gel
1	0	0	gel in 20 min	no gel
1	1	0	gel in 25 min	no gel
1	0	1	gel in 25 min	no gel

[a] Yield after 15 h of reaction.

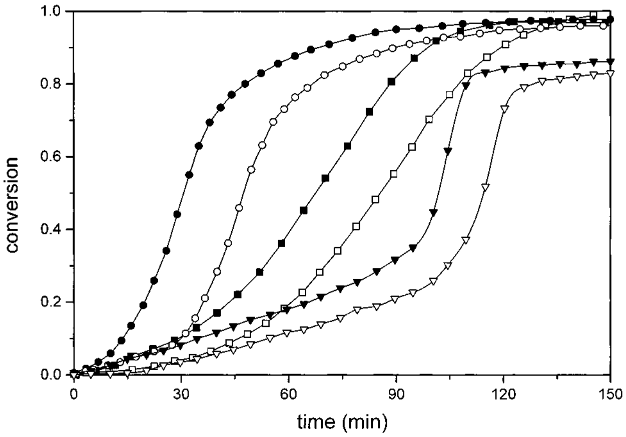
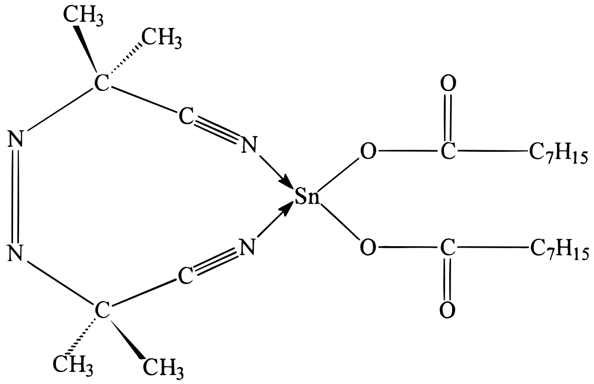


Figure 5. Conversion−time curves for copolymerization of MMA with TRIM at 60 °C, using 1 wt % AIBN, in the absence (open symbol) or in the presence (full symbol) of 1 wt % SnOc$_2$ in 34 wt % ethyl acetate (□, ■); in 34 wt % polyoxypropylene glycol, MW 2000 g/mol (○, ●); in bulk, without TRIM (▽, ▼).

given by Imoto et al.[37] involves the formation of a complex between zinc chloride (ZnCl$_2$) and MMA. In a similar way, for acrylonitrile, Gaylord et al.[38] proposed a ZnCl$_2$:CN complex obtained by electron transfer. The influence of metal halides as complexing agents on the polymerization rate was studied by electron spin resonance (ESR), and Russian authors[39−41] have shown that a molecular complex enhanced the monomer reactivity and affects every polymerization rate constant. Several studies concerning similar interactions between nitrile groups of AIBN and organometallic compounds are reported in the literature.[42−44] Formation of complexes between organotin(II) compounds and nitriles or carboxyls is also reported,[15,36] but no detailed study related to the couple AIBN/SnOc$_2$ was found. Meyer[36] observed that the presence of stannous octoate will reduce the gelation time of cross-linking copolymerization of MMA initiated by AIBN, but no explanation was given. Bamford and Tipper[42] investigated the thermal decomposition of AIBN at 70 °C in the presence of silver perchlorate (AgClO$_4$). They have found that the initiation efficiency of the polymerization of MMA was increased but that the propagation and termination rate constants were not affected.[43] The synergistic effect of AgClO$_4$ was explained by the formation of a cyclic complex that has been isolated.

Scheme 1



Since the acceleration of the formation of linear and cross-linked PMMA concerns the initiation period of the free-radical reaction, the explanation of our results would be a synergistic effect of the particular couple AIBN/SnOc$_2$ due to the formation of a cyclic complex. In such a 1:1 complex (Scheme 1), the N═N azo linkage is tightened, and this facilitates, at a given temperature, the dissociation of the complexed AIBN, compared to pure AIBN.

Conclusions

A synergistic effect of the system AIBN/SnOc$_2$ on free-radical polymerization of methyl methacrylate was emphasized from the determination of the gelation time. Contrary to organotin(IV) compounds such as DBTDL or DBTEH, the presence of SnOc$_2$ in association with AIBN induces a significant increase of the reaction rate, especially at room temperature, a temperature at which AIBN does not decompose (in the absence of light) into radicals. Kinetic measurements have shown that only the initiation rate of polymerization is concerned and that propagation and termination are unaffected by the presence of the organotin(II) compound. Our results are consistent with the formation of a cyclic complex by coordination of the nitrile groups with tin, inducing strained linkages and consequently enhanced dissociation of the azo bond. Confirmation studies of the formation of a cyclic 1:1 complex were undertaken by the determination of the rate of decomposition of AIBN in the presence of various amounts of SnOc$_2$ and will appear in a subsequent paper.

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