Polydimethylsiloxane/poly(methylmethacrylate) interpenetrating polymer networks: 1. Efficiency of stannous octoate as catalyst in the formation of polydimethylsiloxane networks in methyl methacrylate

X. W. He*, J. M. Widmaier*‡, J. E. Herz† and G. C. Meyer*
Institut Charles Sadron
** Ecole d'Application des Hauts Polymères, 4, rue Boussingault F-67000 Strasbourg, France*
† Centre de Recherche sur les Macromolécules, 6, rue Boussingault F-67000 Strasbourg, France
(Received 3 June 1988; accepted 14 July 1988)

Deactivation of the polycondensation catalyst in *in situ* sequential syntheses of polydimethylsiloxane/poly(methyl methacrylate) interpenetrating polymer networks was observed, which impeded the gelation of the elastomeric network. The loss of catalytic activity could be ascribed to the simultaneous presence of radicals and oxygen in the reaction medium. When either oxygen is excluded or a radical inhibitor added, the polycondensation proceeds to gelation at the expected rate.

(Keywords: interpenetrating polymer networks; polydimethylsiloxane; stannous octoate; gelation; inhibitor)

INTRODUCTION

Interpenetrating polymer networks (IPNs) represent an interesting approach to the blending of two polymers[1-3]. In these materials, the constituents are physically entangled in the form of their networks. In contrast to other polymer blends, the state of phase separation obtained at the end of their synthesis cannot change by ageing or under applied stresses, so that the properties are not influenced by such parameters. IPNs are therefore well suited when combination of two polymers is necessary to obtain a material with a specific range of properties. Silicone-containing polymers are particularly incompatible with all other polymers, and a classical mechanical blend would be most unstable, whereas the corresponding IPN provides stable morphology and properties.

Polydimethylsiloxane (PDMS) shows several interesting properties[4] such as low surface tension, oxygen permeability and biocompatibility[5], but, as an elastomer, its mechanical properties are poor, even after crosslinking. IPN systems containing PDMS and a rigid polymer are seldom reported in the literature[6-10]. Among others[11-13], IPNs based on PDMS and poly(methyl methacrylate) (PMMA) have been synthesized in our laboratory. The PDMS network is formed by a polycondensation reaction[14,15] between α,ω-dihydroxy polydimethylsiloxane and a multifunctional alkoxysilane; the rigid network is obtained by radical copolymerization of methyl methacrylate with a trimethacrylate. The synthesis is made on an *in situ* sequential mode: all the reagents of the two systems are mixed together, then the PDMS network is formed first at room temperature and then by copolymerization of the methacrylic monomers by raising the temperature. This method of preparation is the most convenient for industrial purposes, and therefore the only one investigated here.

However, an unexpected difficulty arose in the first experiments, in which gelation of the reaction medium did not take place, indicating that the PDMS network could not form properly. Because an increase in catalyst concentration somehow accelerates gelation, we concluded that the catalytic action of the compound used might have been inhibited. Also, an influence of the catalyst on vinyl groups had already been observed in polyurethane/PMMA IPNs[16], so that at first this hypothesis seemed acceptable. In this paper, we report on a study of the origin of the deactivation of stannous octoate used as catalyst, and a means of protection of its catalytic action.

EXPERIMENTAL

Materials

A list of the materials used in this work is given in *Table 1*. Before use, α,ω-dihydroxy polydimethylsiloxane was heated at 80°C under vacuum for 24 h to eliminate the low molecular weight cyclic compounds. Characterization by gel permeation chromatography (g.p.c.) and vapour pressure osmometry gave a number average molecular weight of 4200 g mol^{-1}. Methyl methacrylate and 1,1,1-trimethylolpropane trimethacrylate (TRIM) were stored

‡To whom correspondence should be addressed

0032-3861/89/020364-05$03.00

over 0.4 nm molecular sieves, but not otherwise freed from inhibitor. The solvents were distilled before use.

Polydimethylsiloxane network formation

PDMS networks were prepared in bulk, in solvent or in methyl methacrylate according to *Scheme 1*. The reaction was carried out under stoichiometric conditions, i.e. [SiOEt]/[SiOH] = 1, at room temperature. The test tubes were left for 2 d, after which the networks were removed. No special care was taken against oxygen. The concentrations and compositions involved are expressed as percentages by weight.

Extraction and swelling measurements

The extraction ratio of PDMS networks, defined as the weight fraction of the soluble material, was measured after 7 d of continuous extraction with ethyl acetate by means of a Soxhlet apparatus. Swelling measurements were carried out in toluene at room temperature. The solvent was renewed three times during the 5 d swelling. In fact, the swelling had practically attained its equilibrium after 48 h. The extent of swelling is characterized by Q_w, the ratio of the weight of the network at equilibrium swelling to the weight of dried polymer.

RESULTS AND DISCUSSION

In the first set of experiments, polydimethylsiloxane networks were synthesized at various precursor concentrations in ethyl acetate, which is a good solvent for all the constituents and miscible with PDMS in any proportion at room temperature. The gelation time, measured as a function of the concentration of PDMS, is given in *Figure 1*. It increases with the dilution of the reaction medium, and below about 25% PDMS no gelation occurs. For higher concentrations, the time to gel is 30 min or less at room temperature. Such behaviour is quite general, since with decreasing precursor concentration the probability of encounter also decreases until a point where no more reaction is possible. On the other hand, a quantitative reaction is never obtained under the present experimental conditions since the condensation product of the reaction is not removed. The amount of extractable species (*Table 2*) and the equilibrium swelling degree (*Figure 2*) confirm the results of gelation by showing that networks with more and more defects are formed as the dilution of the reaction medium increases.

Table 1 Materials

Code	Description	Source
PDMS	α,ω-Dihydroxyl polydimethylsiloxane $\bar{M}_n = 4200\ g\ mol^{-1}$ polydispersity index = 2.5	Wacker
TOES	Tetraethyl orthosilicate	Merck
OcSn	Stannous octoate; 29.1% tin	Goldschmidt
Styr	Styrene; 20 ppm MEHQ	Merck
MMA	Methyl methacrylate 15 ppm hydroquinone	Fluka
TRIM	1,1,1-Trimethylolpropane trimethacrylate 100 ppm methyl hydroquinone	Degussa
AIBN	2,2′-Azoisobutyronitrile	Merck
BPO	Benzoyl peroxide	Merck
TBPC	4-Tert-butyl pyrocatechol	Merck
DBPC	2,6-Di-tert-butyl-4-cresol	Fluka
EtAc	Ethyl acetate	Merck
Tol	Toluene	SdS

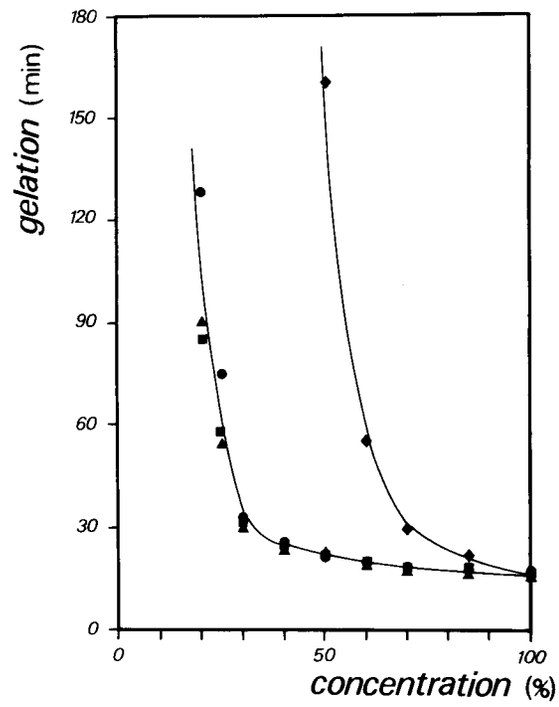

Figure 1 Gelation time of polydimethylsiloxane in the presence of 2.5% stannous octoate *versus* PDMS concentration in various reaction media: ▲, ethyl acetate; ◆, MMA; ●, MMA+0.1% TBPC; ■, MMA+5% TRIM+0.5% AIBN+0.1% TBPC

Scheme 1

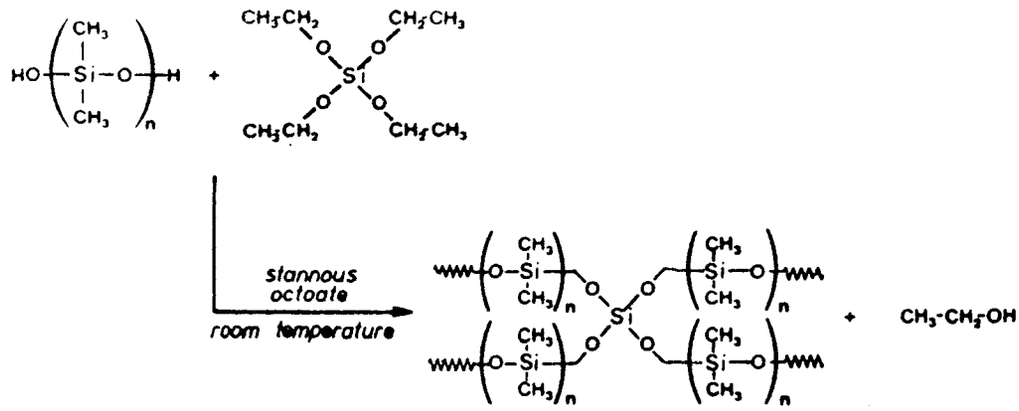

Table 2 Characteristics of PDMS networks prepared at various dilutions in ethyl acetate

PDMS (%)	Sol fraction (%)	Q_w[a]
100	2.49	3.1
85	2.99	3.6
70	3.72	4.2
60	4.33	4.7
50	5.96	5.5
40	8.11	6.9
30	12.3	10.3

[a] In toluene

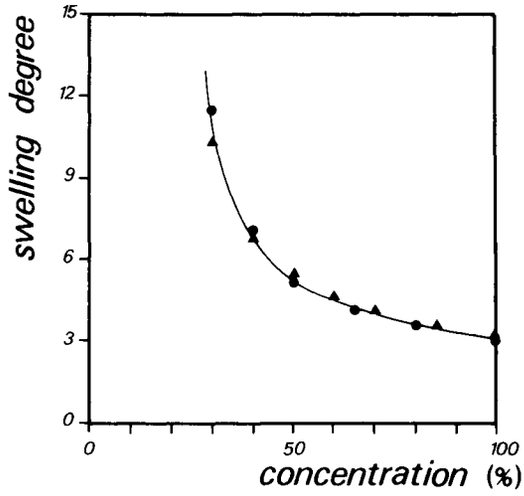

Figure 2 PDMS weight swelling degree in toluene *versus* PDMS concentration for networks prepared in ethyl acetate (▲) and in MMA+0.1% TBPC (●)

By replacing ethyl acetate by methyl methacrylate in otherwise unchanged experimental conditions, gelation is delayed, and this effect becomes more pronounced with increasing dilution; see *Figure 1*. Below 50% PDMS, the polycondensation is stopped before gelation. Apparently, the catalytic action of stannous octoate is somehow influenced by methyl methacrylate, but not by ethyl acetate. Thus, with 2.5% catalyst, gelation in methyl methacrylate is about 8 times slower than in ethyl acetate for 50% PDMS concentration. However, with 1% catalyst concentration, the difference in reactivity of the two media is even more pronounced, since the network forms within one hour in ethyl acetate whereas no gel is obtained in the monomer. Therefore, only a part of OcSn is inactivated, and if the concentration of catalyst exceeds this amount, the reaction may proceed. A last observation (*Figure 3*) can be made from the effect of a mixture of ethyl acetate and methyl methacrylate on the gelation time. For less than 33% methyl methacrylate, the time to gel remains low, but above this value, it increases very rapidly. All these observations indicate a possible interaction between the double bond of the monomer and stannous octoate, which tends to deactivate the catalyst of PDMS network formation. The fact that the vinyl group may be involved seems further substantiated by the use of styrene (*Table 4*), which shows the same behaviour.

The origin of deactivation may therefore be due to the formation of a complex between monomer and catalyst. However, the deactivation process is progressive and not instantaneous, since gelation can be achieved after longer periods, say several days. On the other hand, deactivation is important or complete only in a large excess of methyl methacrylate with respect to stannous octoate: at the transition value obtained in *Figure 3*, a complex would consist of 100 molecules of methyl methacrylate and 1 molecule of OcSn, which is impossible. A direct interaction between the monomer and the catalyst therefore seems to be excluded.

Another hypothesis is the action of the radicals, which are present in the reaction medium, on stannous octoate. Radicals may originate from methyl methacrylate, AIBN or oxygen if air is not eliminated. In this case, the action of AIBN on OcSn was tested under different experimental conditions. At room temperature, the presence of various amounts of AIBN has no influence on the gelation time of PDMS in ethyl acetate (*Figure 4*). When heated to 60°C, a temperature at which AIBN decomposes readily into

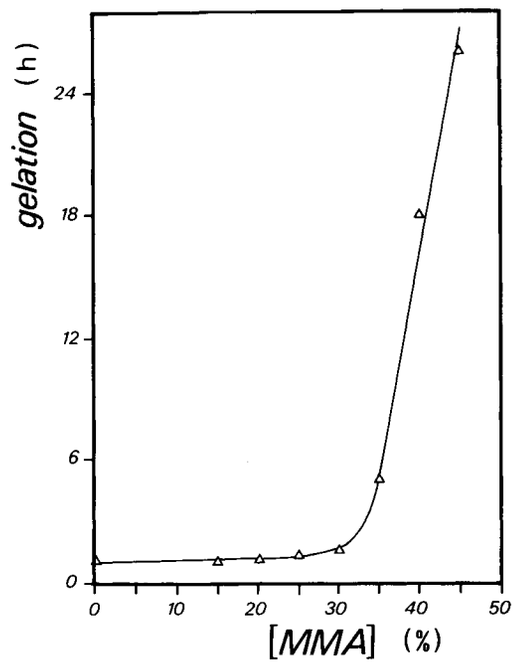

Figure 3 Gelation time of polydimethylsiloxane in a mixture of ethyl acetate and methyl methacrylate *versus* MMA concentration. PDMS/solvent = 50/50; OcSn concentration = 1.25%

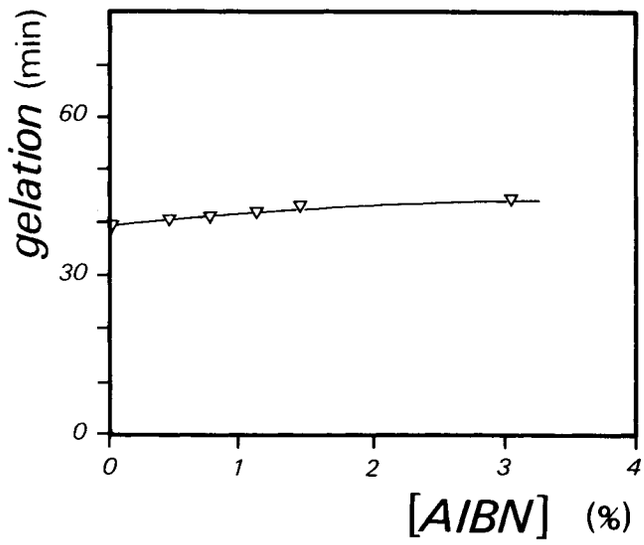

Figure 4 Gelation time of polydimethylsiloxane in ethyl acetate *versus* AIBN concentration. PDMS/EtAc = 50/50; OcSn concentration = 1.7%

Table 3 Effect of radicals on gelation of PDMS catalysed with 2% stannous octoate

Solvent[a]	Generator of radicals[b]	Time to gel[c] (min)
EtAc	–	17.5
EtAc	AIBN	300
Tol	–	14
Tol	BPO	No gel

[a] PDMS + TOES/solvent = 50/50
[b] Initiator concentration = 2%; radicals obtained after 30 min at 60°C (AIBN) or 80°C (BPO)
[c] At room temperature

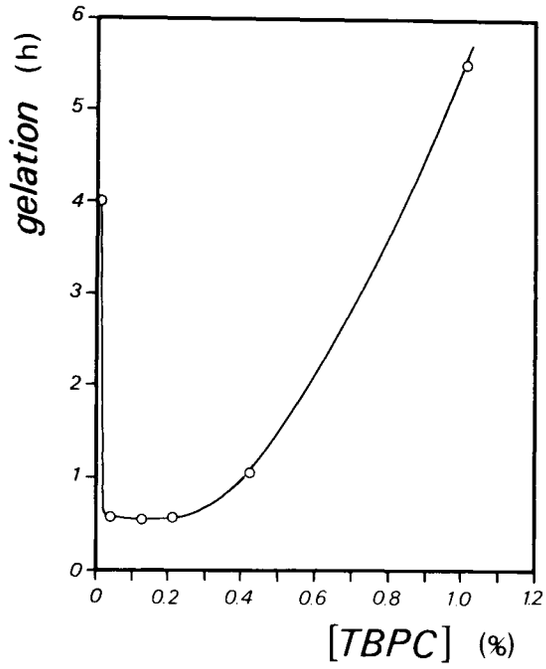

Figure 5 Gelation time of polydimethylsiloxane in methyl methacrylate *versus* TBPC concentration. PDMS/MMA = 50/50; OcSn concentration = 2.0%

radicals, the time to gel increases from 17.5 min to 300 min (*Table 3*). Radicals issued from benzoyl peroxide, another classical initiator, have a similar inhibitory effect: no gel at all is obtained upon its decomposition.

These results clearly demonstrate that the origin of the catalyst deactivation involves radicals, so that, conversely, the addition of a radical inhibitor to the reaction medium should prevent such an effect. To test this assumption, a small amount (0.1%) of 4-tert-butyl pyrocatechol (TBPC) was added to the methacrylic monomers. As a consequence, the gelation time became identical to that observed in ethyl acetate. Thus the catalytic activity of stannous octoate is influenced by radicals and protected by the addition of inhibitors. It has been verified that TBPC alone does not catalyse the polycondensation, and its influence at various concentrations on gelation is displayed in *Figure 5*: the gelation time decreases with increasing TBPC concentration up to ≈0.3%; for higher inhibitor contents, it increases again, but this increase is due to the precipitation of OcSn which occurs under these conditions, and not to another deactivation effect.

The networks formed in the presence of methyl methacrylate containing TBPC show the same swelling behaviour as those formed in ethyl acetate (*Figure 2*); therefore a minimal amount, less than 0.2%, of TBPC is sufficient to prevent deactivation of the catalyst, and does not introduce further defects in the networks. Finally, several other inhibitors have been tested (*Table 4*) to generalize the above results: the protection effect is obvious in each case. Also, our conclusions hold for styrene.

The role of oxygen radicals has already been mentioned, and stannous octoate containing bivalent tin is also subject to oxidation. As above, in a new set of experiments, the gelation time was measured in ethyl acetate in the absence of oxygen. The result shows that with or without radicals from AIBN, gelation occurs in about 18 min, indicating no deactivation. Compared to the 300 min found when both air and AIBN are present (*Table 3*), this result proves that neither oxygen nor radicals alone has any effect on gelation. Both must be present to induce a deactivation of OcSn, and a probable mechanism may be the following:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} \rightarrow RO^{\bullet} + {}^{\bullet}O^{\bullet}$$

$${}^{\bullet}O^{\bullet} + Sn(OOCC_7H_{15})_2 \rightarrow OSn(OOCC_7H_{15})_2$$

$$RO^{\bullet} \rightarrow R^{\bullet} + {}^{\bullet}O^{\bullet} \quad \text{or} \quad RO^{\bullet} + O_2 \rightarrow ROO^{\bullet} + {}^{\bullet}O^{\bullet}$$

According to this scheme, stannous octoate is oxidized and the resulting stannic derivative does not have any catalytic action on the polycondensation. Also, it follows that a radical can deactivate several catalytic molecules, thus corroborating earlier experimental observations[16]. *Table 4* summarizes the results: a gelation time similar to that in ethyl acetate may be obtained in methyl methacrylate by two means: the addition of an inhibitor as radical captor, or the exclusion of oxygen from the reaction medium. Obviously, the former is easier to apply in synthesis of PDMS/PMMA IPNs, and also, more generally on an industrial scale.

CONCLUSION

When polydimethylsiloxane networks are prepared in the presence of monomers able to undergo radical

Table 4 Effect of oxygen and various inhibitors on PDMS network formation with stannous octoate as the catalyst

System[a]	OcSn (%)	Inhibitor		Time to gel (min)
		Name	Concentration (wt%)	
PDMS/EtAc	2.5	–	–	22
PDMS/MMA	2.5	–	–	160
PDMS/MMA	2.5	[b]	–	19.5
PDMS/MMA	2.5	TBPC	0.1	21.5
PDMS/MMA	2.5	Hydroquinone	0.1	24
PDMS/MMA	2.5	Benzophenone	0.1	33
PDMS/MMA	2.5	DBPC	0.2	21
PDMS/Styr	1.0	–	–	no gel
PDMS/Styr	1.0	TBPC	0.1	41
PDMS/Styr	2.5	–	–	29

[a] PDMS/solvent = 50/50
[b] Absence of oxygen

polymerization, deactivation of the catalyst can be avoided either by eliminating oxygen from the reaction medium or by adding a radical inhibitor. As an important consequence of this, it becomes possible to synthesize IPNs based on PDMS and vinyl polymers *in situ*, which is the method best suited for industrial preparation of such materials.

ACKNOWLEDGEMENT

X. W. He gratefully acknowledges financial support from CdF-Chimie, Altulor Division.

REFERENCES

1 Klempner, D. *Angew. Chem.* 1978, **90**, 104
2 Lipatov, Y. S. and Sergeeva, L. M. 'Interpenetrating Polymeric Networks', Daukova Dumka, Kiev, 1979
3 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981
4 Noll, W. 'Chemistry and Technology of Silicones', Academic Press, New York, 1968
5 Quinn, K. J. and Courtney, J. M. *Br. Polym. J.* 1988, **20**, 25
6 Sperling, L. H. and Sarge, H. D. *J. Appl. Polym. Sci.* 1972, **16**, 3041
7 Ebdon, J. R., Hourston, D. J. and Klein, P. G. *Polymer* 1984, **25**, 1633
8 Ebdon, J. R., Hourston, D. J. and Klein, P. G. *Polymer* 1986, **27**, 1807
9 McGarey, B. and Richards, R. W. *Polymer* 1986, **27**, 1315
10 McGarey, B. and Richards, R. W. *Br. Polym. J.* 1987, **19**, 111
11 Djomo, H., Widmaier, J. M. and Meyer, G. C. *Polymer* 1983, **24**, 1415
12 Jin, S. R., Widmaier, J. M. and Meyer, G. C. *Polymer* 1988, **29**, 346
13 Nevissas, V., Widmaier, J. M. and Meyer, G. C. *J. Appl. Polym. Sci.* 1988, **36**, 1467
14 Mark, J. E. and Sullivan, J. L. *J. Chem. Phys.* 1977, **66**, 1006
15 Llorente, M. A. and Mark, J. E. *J. Chem. Phys.* 1979, **71**, 682
16 Meyer, G. C. *Makromol. Chem. Rapid Commun.* 1983, **4**, 221