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Thermal crosslinking of poly(methyl methacrylate-*co*-*N*,*N*-dimethylaminopropylacrylamide)

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Summary

Copolymers of methyl methacrylate(MMA) with N,N-dimethylaminopropylacrylamide (DMA) were heated at various temperatures, and their thermal crosslinking was investigated. A copolymer with a compsition of [MMA]/[DMA] = 3 became completely insoluble in chloroform when heated at 180°C for 5 minutes or at 150°C for 20 minutes. Other copolymers containing less than 5 mol % DMA also crosslinked when heated at 170°C for 30 minutes. A mixture of polyMMA with N,N-dimethylaminopropylbenzamide also crosslinked when heated at 170°C. A copolymer of styrene with DMA also crosslinked when heated at above 140°C although the crosslinking was much slower than that of poly(MMA-co-DMA). The formation of imide linkages is proposed as the crosslinking mechanism.

Introduction

Crosslinking of common vinyl polymers has been always an important topic of polymer chemistry because crosslinking improves polymer properties such as thermal stability and mechanical strength. For the polymers containing unsaturated carbon-carbon bonds, vulcanization with sulfur is possible, and for this purpose copolymerization with dienes and divinyl compounds are commonly practiced. However, in some cases the copolymerization with dienes often results in crosslinked polymers, or decrease in some properties such as resistance to oxidation and heat. Other methods to obtain crosslinkable polymers include the copolymerization with comonomers which have crosslinkable groups. Typical examples of such cases are those of acrylic rubbers, where small amounts of monomers containing chloromethyl[1], epoxy[2], nonconjugated dienes[3], etc. are copolymerized with acrylates. Curing is then achieved by heating in the presence of respective crosslinking agents.

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It was found recently in our laboratory that a copolymer of MMA with DMA became insoluble during drying in vacuum at about 60°C, and therefore a few copolymers with different molar ratios were prepared and their thermal crosslinking was studied.

Experimental

MMA(Aldrich) and DMA(Monomer Polymer Dadjac) were purified by distillation under reduced pressure before use. The copolymerization was carried out at 60°C in benzene using AIBN as initiator. The copolymers were precipitated in hexanes, and purified by reprecipitation from benzene/hexanes. The copolymer compositions were calculated from elemental analysis carried out by Desert

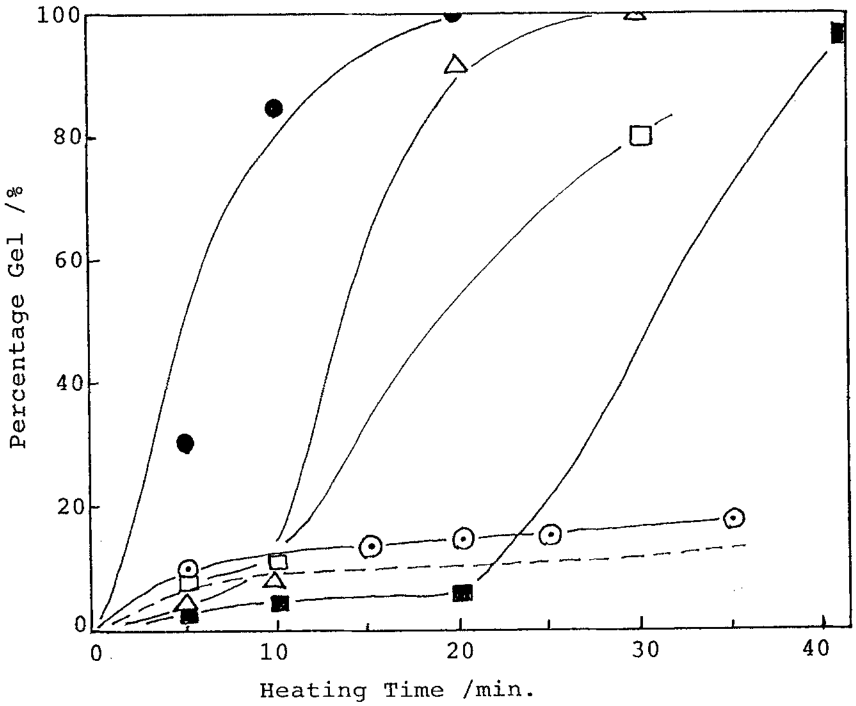


Fig. 1. Thermal crosslinking of poly(MMA-co-DMA).

-------: PolyMMA at 180°C.
—⊙—: Copolymer I at 130°C. —●— : at 160°C.
—■—: Copolymer II at 150°C. —△—: at 160°C.
—□—: Copolymer III at 170°C.

d[MMA]/d[DMA] : Copolymer I = 3.0, II = 11.1, III = 60.

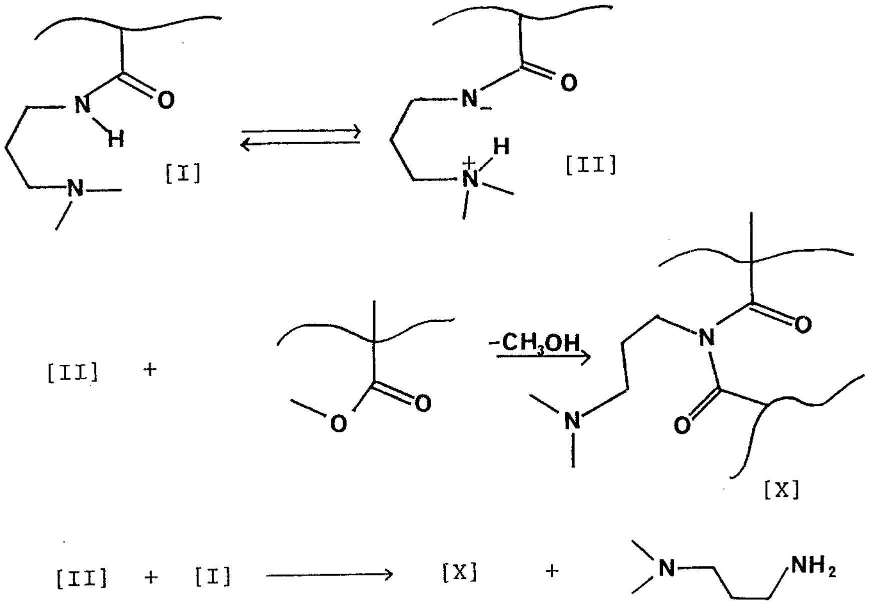
Analytics of Tucson Arizona. The inherent viscosities of the copolymers were determined at 25°C in chloroform. They were found to be in the range of 0.28 - 0.30 dl/g.

The copolymers were heated at different temperatures in test tubes and were stirred in chloroform for over 24 hrs to extract the solubles. The chloroform-insoluble fractions were filtered, dried and weighed.

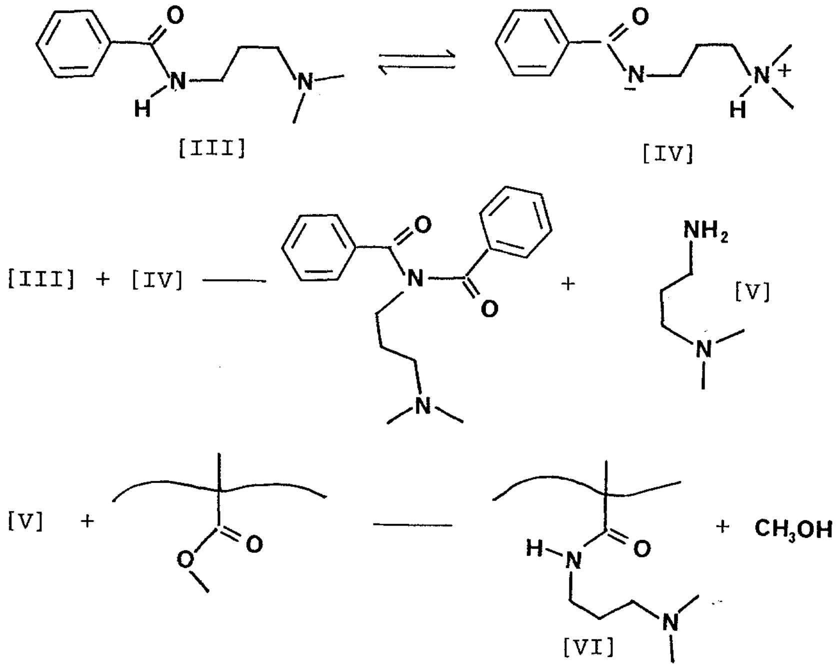
Results and Discussion

Fig. 1 shows the thermal crosslinking behaviors of the copolymers. PolyMMA alone did not crosslink appreciably even at 180°C. Copolymer I became completely insoluble in chloroform after 5 minutes of heating at 180°C. Induction periods seem to exist when heated at lower temperatures, such as below 160°C, and for the copolymers containing smaller amounts of DMA. Little crosslinking took place when heated at 130°C for 35 minutes. From these results it can be said that several mole% of DMA is sufficient to crosslink polyMMA by heating to 160-170°C for 20 - 30 minutes.

A possible mechanism of this crosslinking is proposed in Scheme 1. An imide linkage is thought to be formed as crosslinking bridge.



In order to see if amide-containing tertiry amines would serve as crosslinking agents, polyMMA was mixed with N,N-dimethylaminopropylbenzamide (prepared from benzoylchloride and N,N-dimethylaminopropylamine), and the mixture was heated at 150°C for 1 hr. The polyMMA containing 23% of the benzamide became totally insoluble in dichloromethane after heating. A similar mechanism is proposed for the crosslinking with the benzamide as shown in Scheme 2.



As a result of crosslinking N,N-dimethylaminopropylamine is eliminated which then can react with the ester groups of polyMMA and methanol is eliminated. When polyDMA was heated in vacuum at 160°C in a sealed Pyrex tube,drops of a liquid deposited on the wall of the cool part of the tube, which was confirmed to be N,N-dimethylaminopropylamine from the IR spectra of both liquids.

A copolymer of styrene(ST) with DMA (composition: [ST]/[DMA] = 1.8, and η_{inh}= 0.16 dl/g) was prepared and its thermal crosslinking behavior is shown in Fig.2. It can be seen that the crosslinking of the ST copolymer is much slower than that of the MMA copolymers, because the former lacks ester groups which is attacked by the imino anion[II] (see Scheme 1).

It is concluded that tertiary amine-containing amides can be useful crosslinking agents for polyacrylates and polymethacrylates. Further studies on this diemethylaminoalkylamide-crosslinking of acrylic polymers are in progress.

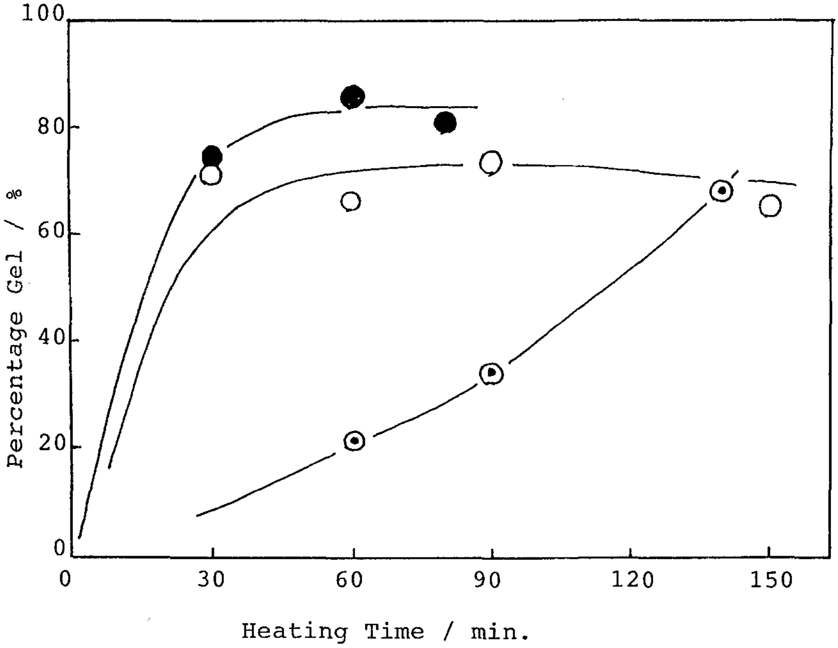


Fig. 2. Thermal crosslinking of poly(ST-co-DMA).
⊙ : 140°C, ○ : 160°C, ● : 180°C
Copolymer composition d[ST]/d[DMA] = 1.8

References

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