Electron Spin Resonance Spectroscopic Studies on Microheterogeneity of Crosslinked Polymers. IV. Correlation between Void Evaluation of Crosslinked Resin and Microgelation in Monomethacrylate/Dimethacrylate Copolymerizations

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ABSTRACT: Electron spin resonance spectroscopic studies on the microheterogeneity of crosslinked polymers were performed to ascertain the correlation of the void evaluation of monomethacrylate/dimethacrylate (DMA) cured resins with the microgel formation before gelation in their crosslinking copolymerizations. Lauryl methacrylate (LMA) was added to methyl MA (MMA)/ethylene DMA (EDMA) copolymerization because the addition of LMA reduces the occurrence of intramolecular crosslinking by the steric hindrance of bulky long-chain alkyl groups, leading to the formation of a less densely crosslinked microgel core and a less microheterogeneously crosslinked resin. Then MMA/vinyl laurate (VL)/EDMA terpolymerization was performed because the polymerizability of conjugated methacryloyl groups belonging to MMA and EDMA is markedly high compared with the unconjugated vinyloxycarbonyl group of VL. Thus, enhanced microheterogeneity for MMA/VL/EDMA terpolymerization would be induced as compared with MMA/EDMA copolymerization. Finally, allyl MA (AMA) and vinyl MA (VMA) crosslinkers were used in place of EDMA because in the polymerizations of AMA and VMA having two types of carbon–carbon double bonds of different reactivities there was no microgelation observed up to the gel-point conversion. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1187–1192, 2001

Key words: electron spin resonance; crosslinked resin; void; microheterogeneity; microgelation; crosslinking

INTRODUCTION

As part of our continuing studies on the elucidation of the 3-dimensional network formation

mechanism in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds,[1] we pursued the process of network formation by electron spin resonance (ESR) spectroscopy, especially focusing on the microheterogeneity of the network structure.[2–4] We performed ESR spectroscopic evaluation of the microheterogeneous network formation processes in the free-radical crosslinking copoly-

merization of methyl methacrylate (MMA) with ethylene dimethacrylate (EDMA) by using copper(II) tetraphenylporphyrin (CuTPP) and copper(II) methacryloyloxyphenyl triphenylporphyrin (CuMAOTPP) as spin probes.[2] We used this method because the segmental motion of the network is changed between the densely and loosely crosslinked structures, and the ESR method has the advantage of being able to study microscopic environments. The CuMAOTPP, which was incorporated into the loosely crosslinked network or immobilized in the densely crosslinked network, is a convenient spin probe and the spectral simulation is useful to semiquantitatively estimate the change of the microscopic environment as the network formation proceeds in the solution copolymerization of MMA with EDMA. Furthermore, the CuTPP spin probe could be a useful tool to evaluate the mobility of low molecular weight molecules in the gelled system; it is excluded from a densely crosslinked network part to a void part, and therefore the change of the cavity of the polymer network would be reflected as the ESR spectral change of CuTPP was excluded therein. The latter result using the CuTPP spin probe was extended to the evaluation of void parts in the microheterogeneously crosslinked resins in the free-radical crosslinking monomethacrylate/DMA copolymerizations.[3] The CuTPP was verified as a useful spin probe for the evaluation of void parts under specified polymerization conditions. The mobility restriction of CuTPP by network formation was noticeably reduced under the conditions introducing the inhomogeneous networks as a result of the exclusion of CuTPP from the densely crosslinked network parts to void ones in cured resins. We also attempted to extend the above discussion to a detailed void evaluation by measuring ESR spectra at lower temperatures by utilizing the interactions between spin probes and side chains.[4] The mobility of CuTPP was quite restricted at lower temperatures, providing a useful tool to allow a detailed evaluation of the void parts.

As an extension of the above ESR spectroscopic discussion of the microheterogeneity of crosslinked polymers,[2–4] the present article deals with the correlation of the void evaluation of monomethacrylate/DMA cured resins by ESR spectroscopy with the microgel formation before gelation in their crosslinking copolymerizations. Because microgelation could be significantly related to the formation of void parts in cured resins under specified polymerization conditions, it would be important as a preformation history of a microheterogeneously cured resin. In this connection, Staudinger and

Huseman[5] reported the formation of a styrene/divinylbenzene microgel. Thereafter, a number of crosslinking polymerization systems were investigated for the occurrence of microgelation in the homopolymerizations of multivinyl compounds and their copolymerizations with monovinyl monomers.[6–10] We also dealt with microgelation by pursuing the change of the dependence of the radius of gyration of the prepolymer on the molecular weight by using indirect[11,12] and direct[13,14] light scattering (LS) methods.

EXPERIMENTAL

Materials and Polymerization

Conventional methods were used to purify MMA, allyl MA (AMA), vinyl MA (VMA), vinyl laurate (VL), lauryl MA (LMA), and EDMA as monomers and 2,2′-azobisisobutyronitrile (AIBN) as the initiator and toluene as the solvent. VMA and VL were supplied by Shin-Etsu Vinyl Acetate Co., Ltd., Japan, and the others were commercially available reagents). The CuTPP was prepared according to the literature.[15]

Polymerization was conducted at 50°C in a manner similar to that reported previously.[16] Thus, the copolymerizations in the presence of CuTPP were carried out for ESR measurements. For example, required amounts of MMA, EDMA, AIBN, and toluene were mixed. Then 1 mg of CuTPP and 1 mL of the toluene solution were put into a glass ampoule equipped with a 5-mm diameter ESR tube. The mixture was degassed on a vacuum line by five freeze–pump–thaw cycles and then sealed under a vacuum. The ampoule was then immersed in a water bath controlled at 50 ± 0.1°C. The polymerization proceeded for 24 h and a completely cured resin was obtained.[3]

ESR Measurement

X-Band ESR measurements were performed on a Jeol FE-1X spectrometer equipped with a temperature control system with a 300 ± 50 mT sweep width, a 0.5-mT modulation, 2-mW microwave power, and a moderate amplitude (100–10,000). The ESR data acquisition and spectral simulation were carried out on a Macintosh Quadra 800 personal computer by using a program that we constructed based on LabVIEW2 (National Instruments Corporation).
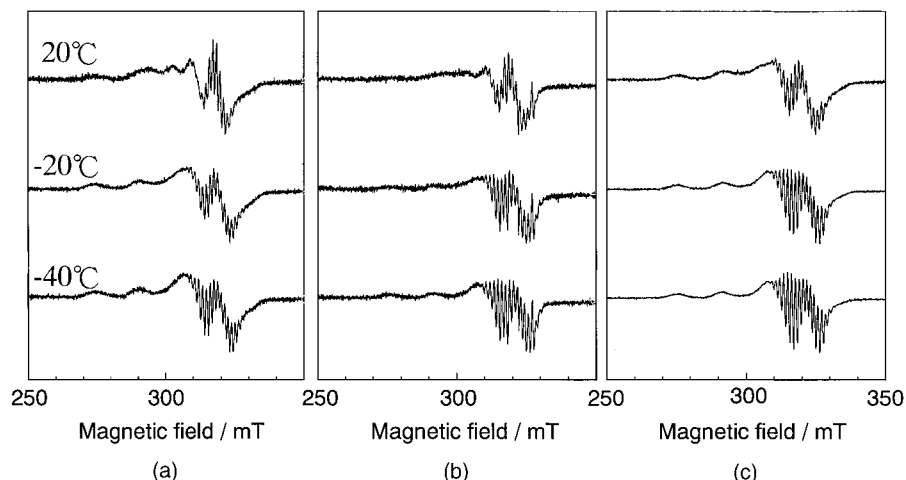
Figure 1   ESR spectra of CuTPP in (a) 70/30 MMA/EDMA copolymerization and (b) 68/2/30 and (c) 65/5/30 MMA/LMA/EDMA terpolymerizations at 20, -20, and −40°C.

RESULTS AND DISCUSSION

Suppressed Microgelation by Steric Effect of Long-Chain Alkyl Groups

In the free-radical crosslinking polymerization and copolymerization of multivinyl compounds the control of microgelation, especially up to the actual gel-point conversion, is very significant because microgelation leads not only to delayed gelation but also to the microheterogeneity of network structures of 3-dimensional polymers, which is closely related to their properties.

We directly pursued the process of microgel formation by using our new technique of LS measurement.[13,14] Thus, the polymerization solution, which was adjusted to a required concentration by adding solvent, was subjected to LS measurement without isolating the resulting prepolymer because the microgel or microgel-like prepolymer could not pass through the micropore filter used for optical clarification; also, the possibility of postpolymerization of the isolated prepolymer was quite high. A significant decrease in the radius of gyration and the second virial coefficient was observed under the polymerization conditions where an occurrence of intramolecular crosslinking leading to microgel formation was expected to be enhanced. The microgelation processes in the homopolymerization of EDMA and its copolymerization with MMA were followed successfully; the correlations between the microgelation and the primary chain length, the content of pendant vinyl groups, the monomer concentration, or solvent were clarified. The microgelation became noticeable with an increase in the primary chain length, an increase in the pendant vinyl content, a decrease in the monomer concentration, and in the good solvent. As an extension of the above work, alkyl MA having a long-chain alkyl group such as LMA or stearyl MA was added to a MMA/EDMA copolymerization system.[17] The addition of LMA reduces the occurrence of intramolecular crosslinking by the steric hindrance of bulky long-chain alkyl groups and leads to the formation of a less densely crosslinked microgel core. This steric effect would lead to the formation of a less microheterogeneously crosslinked resin.

Here it should be recalled that in MMA/EDMA (70/30 molar ratio) solution copolymerization in toluene at a dilution of 2/3 in the presence of a CuTPP spin probe there was no hyperfine structure detected at around 315 mT for the ESR spectra of CuTPP measured at 20°C.[3] This was attributed to the formation of a microheterogeneously crosslinked resin with bigger voids[3] because the appearance of the hyperfine structure corresponded to the restricted motion of CuTPP.[2,18]

Thus, MMA/LMA/EDMA (68/2/30 and 65/5/30 molar ratios) solution terpolymerizations were carried out in toluene at a dilution of 2/3 in the presence of 1.5 mmol/L of CuTPP using 1.6 mmol/L of AIBN at 50°C. The terpolymerizations proceeded for 24 h until the completion of polymerization. Figure 1(a–c) shows the ESR spectra of CuTPP at 20, −20, and −40°C for 70/30 MMA/EDMA and 68/2/30 and 65/5/30 MMA/LMA/EDMA solution co- and terpolymerizations, re-

spectively. The appearance of the hyperfine structure at around 315 mT in the ESR spectra for MMA/LMA/EDMA terpolymerizations became clearer with an increasing amount of LMA added in place of MMA. This could be ascribed to the reduced occurrence of intramolecular crosslinking by the steric hindrance of the lauryl group that leads to the formation of a less microheterogeneously crosslinked resin, which was our expectation.

Enhanced Microheterogeneity as Result of Poor Copolymerizability

In our previous article[19] diallyl phthalate (DAP) was cocured in bulk with vinyl monomers having long-chain alkyl groups, including VL, dioctyl fumarate, LMA, and stearyl MA. Thus, for the DAP-LMA copolymerization process leading to microgel formation[20] the initially obtained copolymers or precopolymers of high LMA content, which was a reflection of the high polymerizability of LMA compared with DAP, were not compatible with DAP-enriched polymer chains that rapidly increased with the progress of polymerization. Therefore, they may have predominantly existed in the spaces between the microgels and acted as flexible crosslinkers of the microgels to form a macrogel. This type of microheterogeneous copolymerization of DAP with vinyl monomers having long-chain alkyl groups was further applied for bulk copolymerization systems to obtain direct evidence to support the idea of the microheterogeneity of the systems beyond the gel-point conversion.[21] Also, the solution copolymerization of diallyl terephthalate (DAT) was explored to demonstrate the incompatibility of the initially obtained precopolymer with a high content of comonomer units with DAT-enriched polymer chains.[22]

In this work the above discussion of microheterogeneous copolymerization leading to the microheterogeneity of the crosslinked polymer was extended to the MMA/VL/EDMA terpolymerization. Because the polymerizability of conjugated methacryloyl groups belonging to MMA and EDMA is markedly high compared with a vinyloxycarbonyl group of VL as an unconjugated vinyl group, enhanced microheterogeneity for MMA/VL/EDMA terpolymerization would be induced as compared with MMA/EDMA copolymerization; consequently, long-chain lauryl groups would predominantly exist in the void spaces.
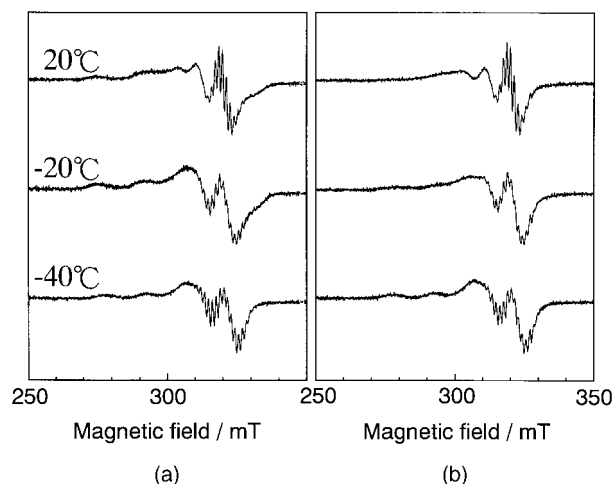

Figure 2 ESR spectra of CuTPP in (a) 68/2/30 and (b) 65/5/30 MMA/VL/EDMA terpolymerizations at 20, −20, and −40°C.

Thus, 68/2/30 and 65/5/30 MMA/VL/EDMA solution terpolymerizations were carried out in toluene at a dilution of 2/3 in the presence of 1.5 mmol/L of CuTPP using 1.6 mmol/L of AIBN at 50°C. Figure 2(a,b) shows the ESR spectra of CuTPP at 20, −20, and −40°C for 68/2/30 and 65/5/30 MMA/VL/EDMA terpolymerizations. These spectra were compared with those for 70/30 MMA/EDMA copolymerization [Fig. 1(a)]. The hyperfine structure at around 315 mT in the ESR spectra disappeared in MMA/VL/EDMA terpolymerization as a reflection of the enhanced microheterogeneity of the crosslinked resin because of poor copolymerizability of the growing methacrylyl radical toward the vinyloxycarbonyl group of VL. Moreover, the presence of nonpolar lauryl groups in the void parts may have had an additional effect on the disappearance of the hyperfine structure in the spectra of CuTPP.

Less Microheterogeneously Crosslinked Resins Using Unsymmetrical Divinyl Compounds with Different Reactivities as Crosslinkers

In the polymerizations of AMA and VMA,[23,24] which have two types of carbon–carbon double bonds, in which the polymerizability of the conjugated methacryloyl group was markedly high compared with the allyl or vinyloxycarbonyl group as an unconjugated vinyl group, no microgelation was observed up to the gel-point conversion. This was a reflection of the low reactivity of the growing methacrylyl radical toward the
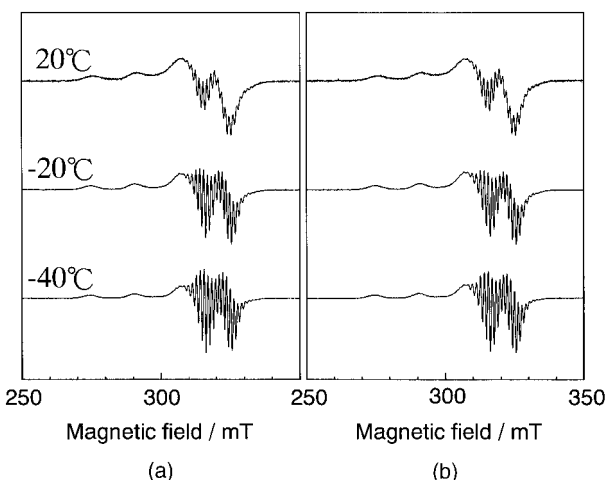
Figure 3 ESR spectra of CuTPP in (a) 70/30 MMA/AMA and (b) 70/30 MMA/VMA copolymerizations at 20, −20, and −40°C.

pendant allyl or vinyloxycarbonyl groups of the prepolymer, resulting in the suppressed occurrence of intramolecular crosslinking. This was quite the opposite of the cases where microgelation easily occurred in the EDMA homopolymerization and MMA/EDMA copolymerization.[11,13,14] The solution polymerizations of AMA and VMA were pursued by LS in comparison with that of EDMA. The double logarithmic plots of the radius of gyration versus the molecular weight for the solution polymerizations of VMA and AMA were close to that for the polymerization of MMA, which provided a linear polymer, and only transparent solutions were obtained. However, in the polymerization of EDMA the plot had the minimum point, corresponding to the turbid point, and the solution turned white. Also, the second virial coefficient (A_2) supported no microgelation in the polymerizations of VMA and AMA, although microgelation was demonstrated in EDMA polymerization as a small A_2 value of less than 10^{-5} mol mL g^{-2}.[14,23]

Thus, 70/30 MMA/AMA and 70/30 MMA/VMA solution copolymerizations were carried out in toluene at a dilution of 2/3 in the presence of 1.5 mmol/L of CuTPP using 1.6 mmol/L of AIBN at 50°C. Figure 3(a,b) shows the ESR spectra of CuTPP at 20, −20, and −40°C for 70/30 MMA/AMA and 70/30 MMA/VMA copolymerizations, respectively. These spectra were then compared with those for 70/30 MMA/EDMA copolymerization [Fig. 1(a)]. The hyperfine structure at around 315 mT in the spectra of CuTPP was clearly detected in the MMA/AMA and MMA/VMA copoly-

merizations. This was ascribed to the formation of less microheterogeneously crosslinked resins, such as AMA and VMA, using unsymmetrical divinyl compounds as crosslinkers with different reactivities.

CONCLUSION

As an extension of a series of ESR spectroscopic studies concerned with the microheterogeneity of crosslinked polymers,[2–4] we discussed the correlation of the void evaluation of monomethacrylate/DMA cured resins with the microgel formation before gelation in their crosslinking copolymerizations, especially focusing on three specified polymerization systems. The LMA was added to the MMA/EDMA copolymerization because the addition of LMA reduced the occurrence of intramolecular crosslinking by the steric hindrance of bulky long-chain alkyl groups, which led to the formation of a less densely crosslinked microgel core.[17] This steric effect led to the formation of a less microheterogeneously crosslinked resin. The discussion of microheterogeneous copolymerization of DAP with long-chain alkyl group vinyl monomers, which led to the microheterogeneity of the crosslinked polymer,[21,22] was extended to a MMA/VL/EDMA terpolymerization. Because the polymerizability of conjugated methacryloyl groups belonging to MMA and EDMA was quite high compared to the unconjugated vinyloxycarbonyl group of VL, an enhanced microheterogeneity for MMA/VL/EDMA terpolymerization was induced as compared with MMA/EDMA copolymerization. Moreover, long-chain lauryl groups predominantly existed in the void spaces. The AMA and VMA crosslinkers were used in place of EDMA to produce a rather homogeneous crosslinked polymer because in the polymerizations of AMA and VMA with two types of carbon–carbon double bonds of different reactivities no microgelation was observed up to the gel-point conversion.[23,24] This was quite the opposite of the cases where microgelation was easy in the EDMA homopolymerization and MMA/EDMA copolymerization.[11,13,14]

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