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Initiator-Free Photo-Emulsion Polymerization of Deuterated Methyl Methacrylate

Tohei Yamamoto[*1], *Tomoaki Saso*[1], *Atsushi Kajiwara*[2]
and Mikiharu Kamachi[3]

[1]Faculty of Engineering, Himeji Institute of Technology, 2167 Shosha,
Himeji 671-2201 Japan
[2]Faculty of Material Science, Nara University of Education,
Takabatake, Nara 630-8301 Japan
[3]Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505 Japan

Summary: Initiator-free Photo-emuslsion polymerization of deuterated methyl methacrylate (MMA-d8) was carried out at 0 °C by using polyoxyethylene nonyl phenylether sodium sulfate (LWZ, Kao Co). After 24 h UV irradiation, poly(MMA-d8) was obtained by 9% yield and the Pn was 4340 on the basis of the intrinsic viscosity in acetone. In the 1H-NMR spectrum of poly(MMA-d8), LWZ fragments were observed and were considered to be bound to the ends of poly(MMA-d8).

Introduction

The authors discovered an intiator-free photo-emulsion polymerization method in the course of study on the synthesis of high molecular weight poly(vinyl alcohol)(PVA)[1~5] by using polyoxyethylene nonyl phenyl ether sodium sulfate (LWZ, Kao Co.) as the emulsifier, and an initiation mechanism shown in Figure 1 was proposed on the basis of following reasults.

The tacticitiy of poly(vinyl acetate)(PVAc) obtained by this method was the same as that of PVAc obtained through radical polymerization. The polymerization was inhibited by oxygen, and ESR signal was observed by irradiation of the frozen VAc/LWZ/methanol system. These facts indicate the polymerization takes place radically. However, as no polymer was obtained by heating the system, initiation by peroxides contained in the system was considered to be negligible. When sodium dodecyl sulfate (SDS) which has no aromatic ring was used as an emulsifier, polymerization did not take place suggesting the necessity of an aromatic ring in the emulsifier. No polymer was obtained by irradiation of a homogeneous

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VAc/LWZ/methanol system suggesting the necessity of micelles to prevent fast quench betweeen pair radicals.

LWZ has very low absorbancy for UV wave and hardly decomposes by UV irradiation. However, once it decomposed, the hydrophilic part is pulled out into water phase, and the hydrophobic part is pulled into the mononomer phase in the micelle to initiate polymerization efficiently. Radicals in the micelle are very few to terminate the reaction and PVAc with a large Pn was obtained. But monomer concentration in the aqueous phase is very low and polymer initiated by hydrophilic radical in the aqueous phase has low molecular weight. In order to confirm the concept shown in Figure 1 the initiator-free photo-emulsion polymerization of deuterated methyl methacrylate (MMA-d8) was examined.

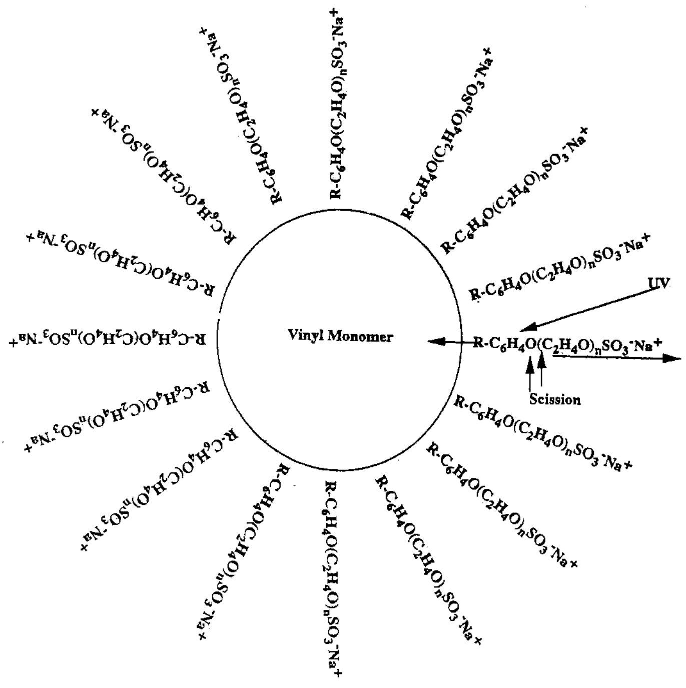

Fig. 1 Initiation mechanism of initiator-free photo-emulsion polymerization of vinyl monomers.

Experimental Part

Materials : MMA-d8 of which undeuterated ratios (analyzed by Wako Pure Chemical Industries LTD) were 0.2%, 0.9% and 0.8% for OCH3, CH2 and CH3, respectively, was purchased from the company was distilled under reduced pressure of nitrogen before use. LWZ was provided from Kao Co and was used without further purification.

Polymerization : In a 30 ml Pyrex Kjeldahl flask were placed 5 ml of MMA-d8, 0.5 ml of LWZ , 10 ml of water and a teflon stirring bar. The mixture was degassed by the freezing-pumping-thawing method and the flask was sealed under vacuum. The flask was placed in a water/ethylene glycol bath at 0 °C, and the mixture was irradiated with a high pressure mercury lamp. After 24 h irradiation, the mixture was poured into 150 ml of water and with stirring Na2SO4 was added gradually until the emulsion broke and poly(MMA-d8) precipitated. After filtration the poly(MMA-d8) was washed with water, reprecipitated from acetone/methanol and dried under vacuum at 60 °C.

Degree of polymerization : Pn of poly(MMA-d8) was determined from the intrinsic viscosity measured in aceton at 30 °C according to the following equation and GPC measurement.

$\log Pn = 3.420 + \log[\eta]$ [6]

NMR analysis : Number of LWZ fragment bound to the polymer ends was estimated by the 1H-NMR spectrum of the polymer shown in Figure 2. The peak assignment of the 1H-NMR spectrum was carried out according to Hatada's paper[7].

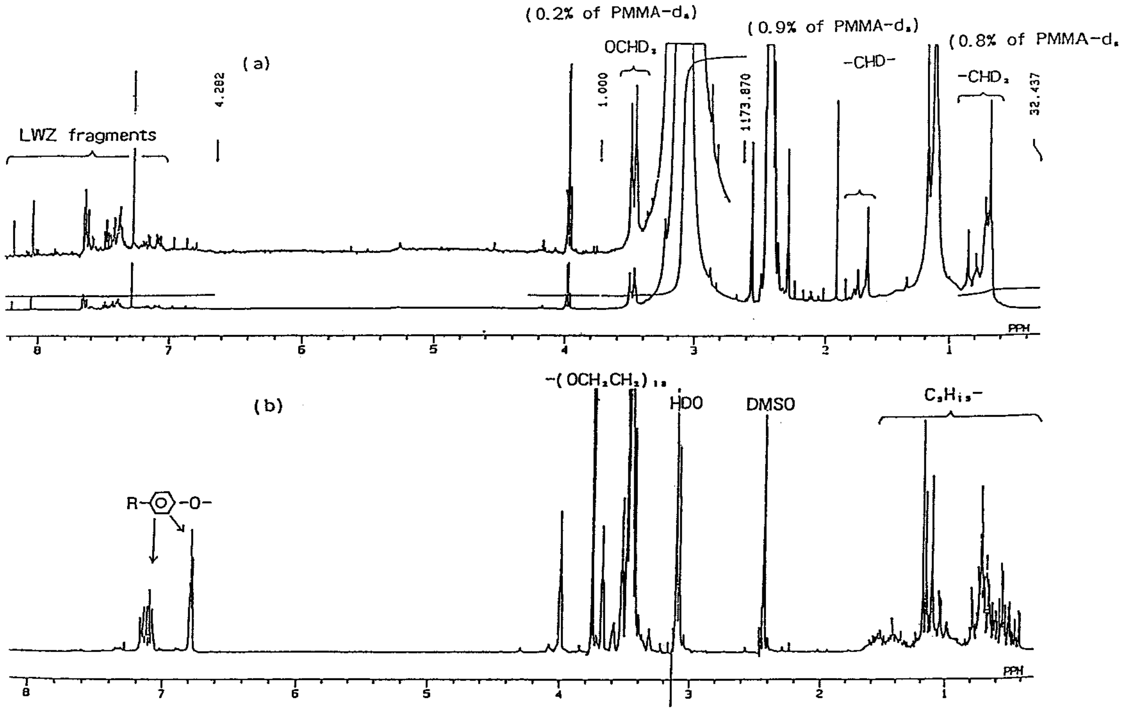

Fig.2 ^{1}H-NMR spectra of (a)PMMA-d_8 and (b)LWZ in DMSO-d_6.

Results and Discussion

Poly(MMA-d8) was obtained in 9% yield, and the intrinsic viscosity of the polymer measured in acetone at 30 °C was 1.65 indicating the Pn to be 4340.1H-NMR of the polymer and LWZ in DMSO-d6 are shown in Figure 2(a) and (b), respectively. Signals by aromatic protons are observed around at 7~8 ppm in Figure 2(a), and as no aromatic compound except LWZ was used through polymerization and purification, the signals were considered to be originated to LWZ. Moreover the chemical shifts are different from those of LWZ in Figure 2(b) and the signals are considered to be those of LWZ fragments bound to the polymer ends not to be residual LWZ. The fragments are considered to be R-C6H5- and /or R-C6H4-O- which have 4 aromatic protons. Hence it is considered that 1.2 LWZ fragments were combined to each poly(MMA-d8) chain from the intensities of the signal of LWZ fragments(4.3) and -CHD2 of poly(MMA-d8) (32.4 : undeuterated ratio=0.8%) and Pn=4340.

The result agrees with the disproportionation ratio (0.6)[8] in the radical polymerization of MMA at 0 °C and the polymerization takes place in the micelle. The fact that LWZ fragments are combined on the polymer ends quantitatively supports the initiation mechanism described above and in Figure 1.

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