

The Studies(II) on the Oxidative Thermal Degradation of Low Molecular Weight Poly(styrene) and Poly(vinylmethylether) Blend

Kim, Sang-Hern

Dept. of Industrial Chemistry Taejon National University of Technology

저분자량 Poly(styrene)과 Poly(vinylmethylether) 블렌드의 열산화에 관한 연구 II

김 상 현

대전산업대학교 공업화학과

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요 약

저분자량($M_w=1970$)을 갖는 poly(styrene)(PS)와 poly(vinylmethylether)(PVME)의 블렌드를 열산화시킬 때 PVME의 분자량 감소 속도는 높은 분자량을 갖는 PS와 PVME의 블렌드를 열산화시킬 때의 PVME 분자량 감소 속도보다 훨씬 느리다. 열산화 과정 동안 PS의 분자량은 변화하지 않았으며 저분자량의 PS의 일부가 산화된 PVME를 분리할 때 함께 녹음을 알 수 있었다. 저분자량의 PS의 모델 화합물로서 2, 4-diphenylpentane을 합성하였고 1%, 5%, 10%의 모델 화합물을 PVME에 첨가하여 열산화시켰다. 이 모델 화합물을 첨가하여 PVME의 열산화를 약간 지연시킬 수 있음을 알 수 있었다.

I. Introduction

The mixture of poly(styrene)(PS) and poly(vinylmethylether)(PVME) was one of the most extensively studied blends.^{1~10)} PVME had been an industrially important water soluble polymer often used as a film-forming additive in coatings. It has been known that PVME is much more susceptible to the thermal oxidation than PS since PVME had the easily abstractable hydrogen due to the electron withdrawing nature of oxygen atom.^{8, 9)} The combination of oxygen as a reactant and heat as an energy source has been a major factor in polymer degradation. Poly(styrene)

exhibited surprising stability relative to other hydrocarbon polymer due to its activating effect of the phenyl group upon the tertiary benzylic hydrogen. It has been suggested that the lack of reactivity arose from shielding effects of the bulky phenyl group.

Recently, Park et al.^{15, 16)} studied the thermal oxidation of blends of PVME and high molecular weight PS(HMPS) by oxygen uptake measurement. It was found that the induction period for oxidation of PVME was lengthened by the presence of PS in the blend. Phase separation occurred shortly before the end of the induction period, and the steady-state rate of oxidation of blend was proportional to the PVME content.

The molecular weight of PVME decreased more slowly in the blend as PS content increased. At the same time PS also underwent chain scission. It was believed that a reaction between PVME radical and PS took place during the induction period resulting in less reactive PS radicals. It was found that the PVME blends with modified styrene containing hydrogen-bonded donors were more effective than PS homopolymer in prolonging the induction period of the thermal oxidation of PVME and in lowering the rate of oxidation in the steady-state region.

The present investigation was an extension of the earlier study to see molecular weight change of low molecular weight PS and PVME. 2, 4-Diphenylpentane was synthesized as a model compound for poly(styrene). This model compound was mixed with PVME to see the oxidation behavior of the mixture of the model compound and PVME.

II. Experimental

1. Material

Poly(vinylmethylether)(PVME) was obtained from the GAF Chemical Corp. In the form of a 50 wt% solution in toluene, and purified by double precipitation from 8%(w/v) toluene solution into an excess amount of hexanes. It was dried in a vacuum oven at room temperature for 7 days. The weight average molecular weight was 120,000 and the polydispersity was 1.26. Styrene monomer was obtained from Aldrich Co. The inhibitor in styrene was removed by an inhibitor removal column (Polyscience Inc.). After removing the inhibitor, calcium hydride was added to the styrene to remove the moisture and stirred for 1 day under nitrogen atmosphere. The final purified styrene was obtained from a middle portion of distillate from vacuum distillation.

2. Polymerization of low molecular weight monodispersed PS

Low molecular weight poly(styrene) was synthesized by anionic polymerization by using sec-butyl lithium (Aldrich Chemical Co., 1.3M solution in hexane) as a initiator. A glass reactor equipped with a sealed mechanical stirrer and 2 inlet tubes with rubber serum stoppers was cleaned, dried, and purged with dry argon gas. Dry cyclohexane (500mL) and 50mL of styrene were introduced into the glass reactor through the syringe needle. After stirring for 20 minutes at 40°C, a precalculated amount of sec-butyl lithium was injected. The polymerization was terminated after 2 hours by adding a small amount of methanol. Poly(styrene) was recovered and purified by using toluene and MeOH. The molecular weight of purified PS was confirmed by GPC. The \bar{M}_w and polydispersity were 1970 and 1.07, respectively.

3. Synthesis of 2, 4-diphenylpentane

Dry magnesium (2.431g) was placed into 250 mL three neck flask equipped with an addition funnel, magnetic stirrer and condenser. The distilled THF was introduced by syringe. 18.507g of α -methylbenzylbromide was added to the magnesium in THF. The reaction continued till the reaction mixture turned dark green. After refluxing for a further 15 minutes, reaction flask was cooled. After quick filtration of the reaction contents the filtrate was placed new three neck flask. 8.693g of dibromomethane was introduced through the addition funnel. The reaction was continued for 2 hours at 80°C. The reaction contents was cooled to room temperature and poured into methanol/water(1:1)(v/v). The precipitate was obtained by filtration. The precipitate was redissolved in THF and added to the methanol/water(1:1)(v/v).

The white product was filtered, and dried overnight in vacuum oven at 90°C. Measured melting point of the obtained 2, 4-diphenylpentane was 123°C.¹⁷⁾ The reaction scheme of 2, 4-diphenylpentane is given in Figure 1.

4. Preparation of polymer blends

A polymer sample was prepared by a solution casting method. Toluene(0.8mL 5%(w/v)) solution was spread evenly on a microscope glass slide. Most of the solvent evaporated in the air in 2 hours : then the sample was transferred into a vacuum oven and dried at room temperature for 4 days and 40°C for 1 day. PVME homopolymer was dried only at room temperature. All samples were kept in a nitrogen atmosphere prior to use.

5. Oxygen uptake measurement

The oxygen uptake measurement apparatus is shown in Figure 2. The amount of consumed oxygen was measured by monitoring the pressure change in a constant volume oxidation cell. Calcium oxide (Aldrich Chemical Co., 99.95%) was placed in the cell to absorb the evolved gases. Pyrex glass wool which was pre-oxidized at 150 °C for more than 2 weeks was used to keep the

calcium oxide away from the sample. The sample cell and empty reference cell, both connected to a pressure transducer (Omega Engineering, Model PX 143-2.5 BD 5V), were placed in an aluminum heating block. The electrical signal from the pressure transducer was transferred to the interface module (Omegarometer, DP200P Process Signal Conditioner, RS232C/RS-485 Converter). The transferred voltage values through the interface were saved on hard disk. In order to establish the temperature equilibrium before oxidation started, both sample and reference cells were filled with N₂ gas and placed in the heating block for 10minutes. After 15minutes of vacuum procedure, pure O₂ gas was introduced into the cells and an initial pressure of 770mmHg was set. Oxidation started at this moment, and all gas delivery lines were closed by rotating the 3-way stopcocks. Each sample was measured at least three times to ensure reproducibility of data.

6. Infrared spectroscopy

A Digilab FTS-60 infrared spectrometer was used to study the FT-IR spectra. All FT-IR spectra were obtained under following conditions : 64 of number of scan, 8cm⁻¹ of resolution, sen-

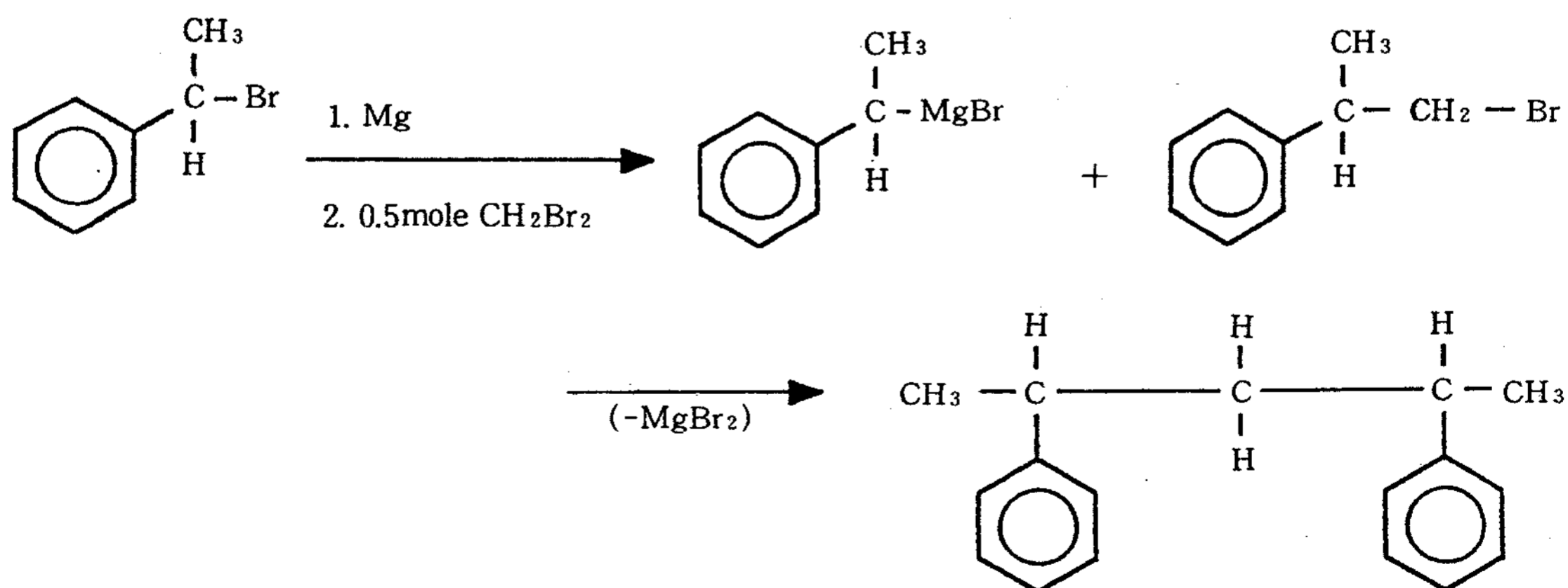


Fig. 1. The synthetic scheme of 2, 4-diphenylpentane.

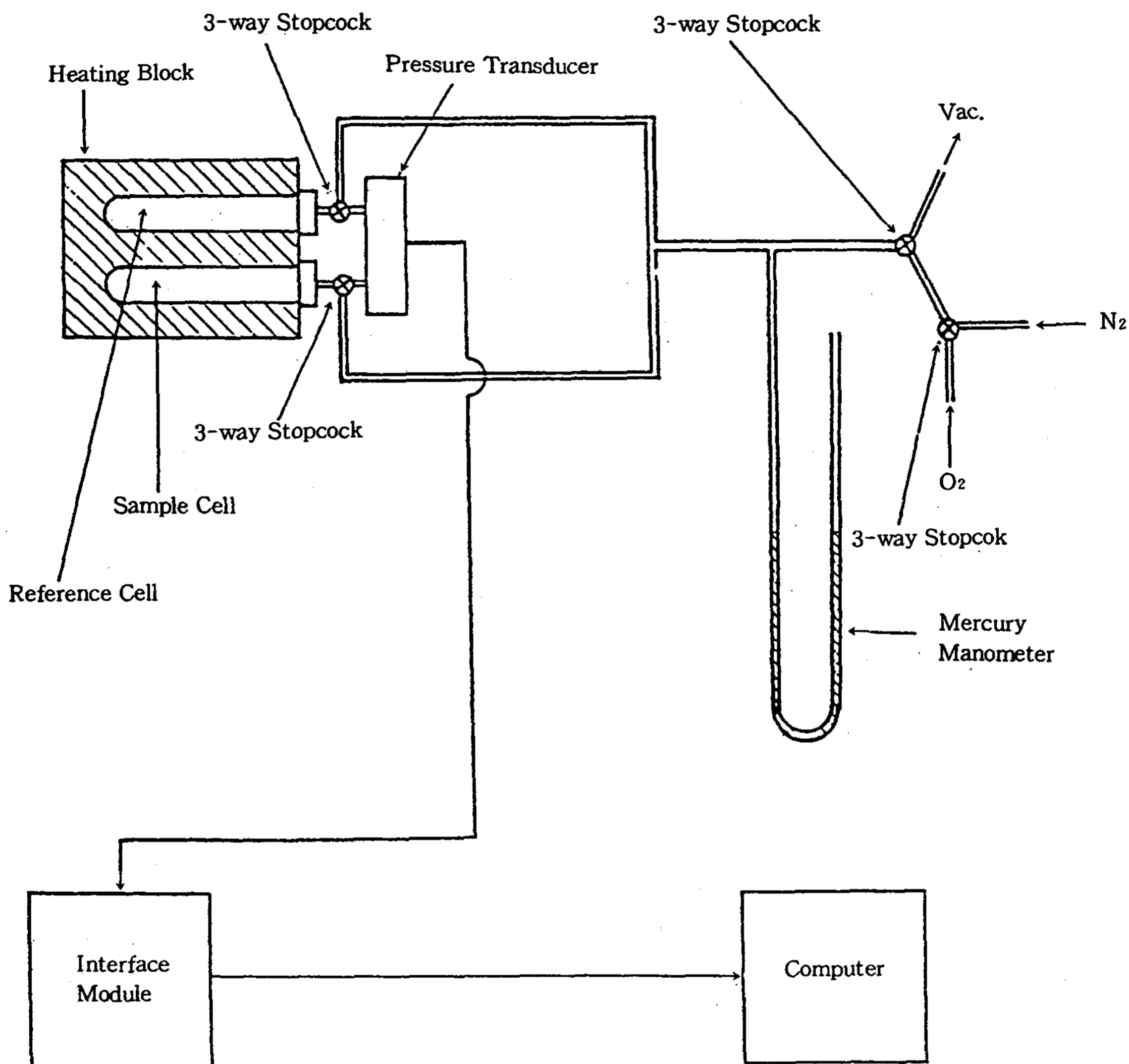


Fig. 2. Schematic diagram of oxygen uptake measurement set-up for thermal oxidation.

sitivity scale of 1.

7. Differential Scanning Calorimetry(DSC)

A Dupont 9,900 thermal analyzer connected with a Dupont 910 differential scanning calorimeter was used for the glass transition temperature(T_g) measurement. DSC samples were prepared by cutting the solvent-cast films into proper sizes. The sample weight was about 10mg. Samples for DSC analysis were scanned at 10°C/

min heating rate from -70°C to 100°C, then cooled at 10°C/min.

8. Separation of LMPS/PVME

An important part of this study was the determination of the chemical and molecular weight changes of PS and PVME in the blend. Therefore, a method was devised to separate the two polymers from each other after oxidation. The procedure takes advantage of the solubility dif-

ference of two polymers : poly(vinyl methylether) is soluble in methanol, which is a nonsolvent for PS. The PVME in the oxidized sample was filtered by using $0.4\mu\text{m}$ porosity filter, and dried in vacuum oven at room temperature for 3 days. The extracts after the first extract were not added to the first extract. Only the first extract was used for the FT-IR and GPC analysis. The obtained precipitated PS was rinsed with at least 10 times.

9. Determination of molecular weight

The molecular weight and molecular weight distribution of the polymer were determined by using a Waters Gel Chromatography(GPC), model 590 with a set of four μ stygel columns ($500, 10^3, 10^4,$ and 10^5 \AA respectively). The elution solvent used was HPLC grade THF and each samples were filled with $0.45\mu\text{m}$ PTFE filters. Injection volume was $50\mu\text{L}$ with a flow rate of $1.0\text{mL}/\text{min}$. The column temperature was kept at 25°C . A differential refractive index detector was used.

10. Ultraviolet spectroscopy

The instrument used was CARY model 2300 spectrophotometer PS and PVME samples were dissolved in THF as a solvent.

III. Results and Discussion

To investigate the chemical structure change of the oxidized PVME separated from blends, the sample separation was attempted by using a precipitation method. The PVME in the oxidized blend was extracted by using methanol as a solvent. The first extract from the oxidized blend was filtered by using $0.4\mu\text{m}$ porosity filter, and dried in vacuum oven at room temperature under a nitrogen atmosphere. The extracts after the first extract was not added to the first extract. The obtained PS precipitate was rinsed

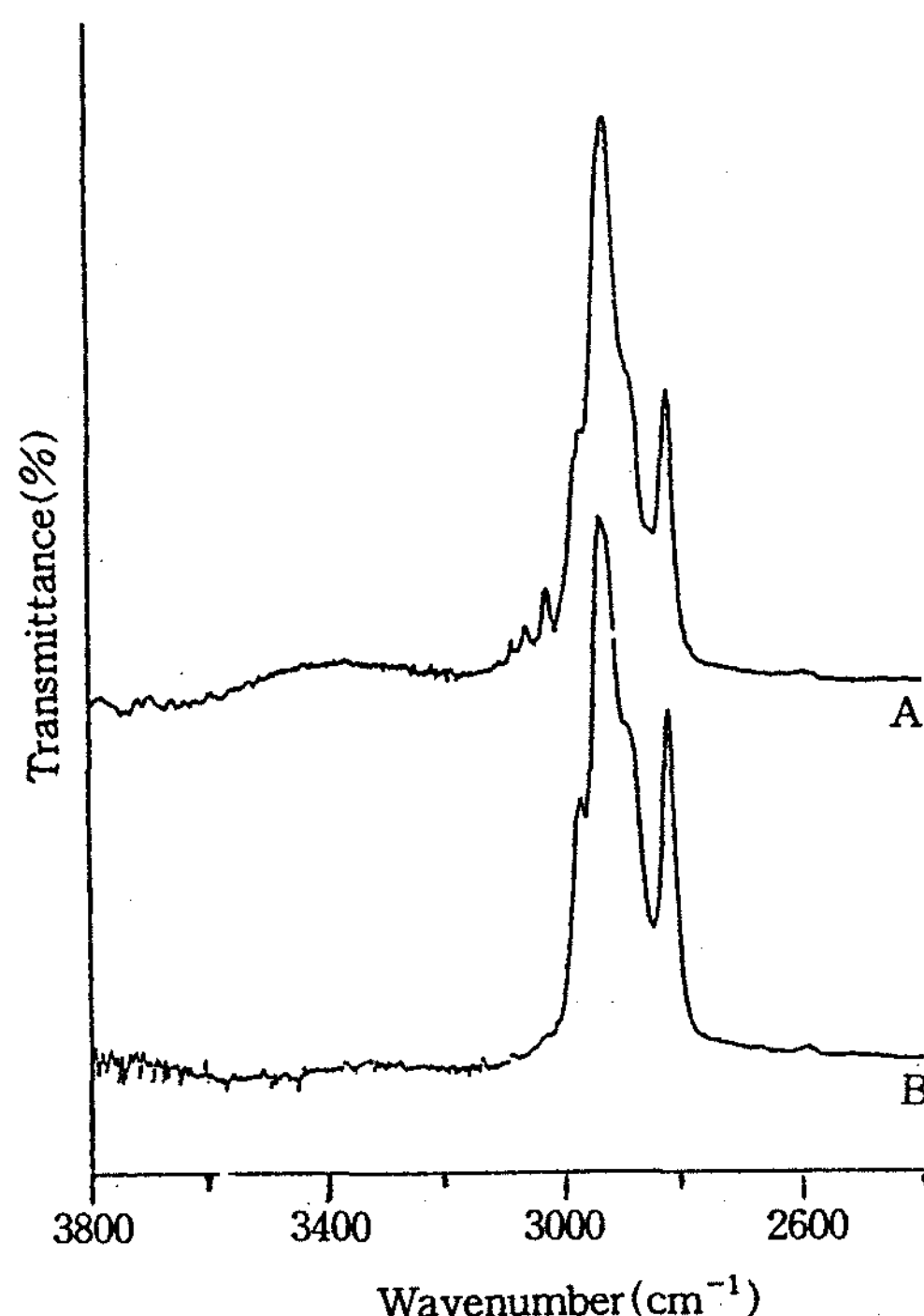


Fig. 3. FT-IR spectra of the extracts from unoxidized(B) and oxidized(A) LMPS/PVME = 50/50 blends.

with methanol at least 10 times. Figure 3 showed the FT-IR spectra of extracts from the unoxidized and oxidized LMPS/PVME = 50/50 blend. The extract from the oxidized blend had small peaks above $3,000\text{cm}^{-1}$ which were due to aromatic C-H stretching. At this moment there may be three possibilities to explain the presence of this aromatic C-H stretching : (1) codissolved PS which was a low molecular weight portion of the added PS in the blend, (2) bonded PS to PVME due to its chemical structure change, and (3) oxidized PS.

To elucidate these possibilities the GPC chromatograms for all blends were checked. Figure 4 shows GPC chromatograms of the extracts from the oxidized LMPS/PVME = 35/65. The extract from the unoxidized blend showed two peaks which corresponded to the original PVME and

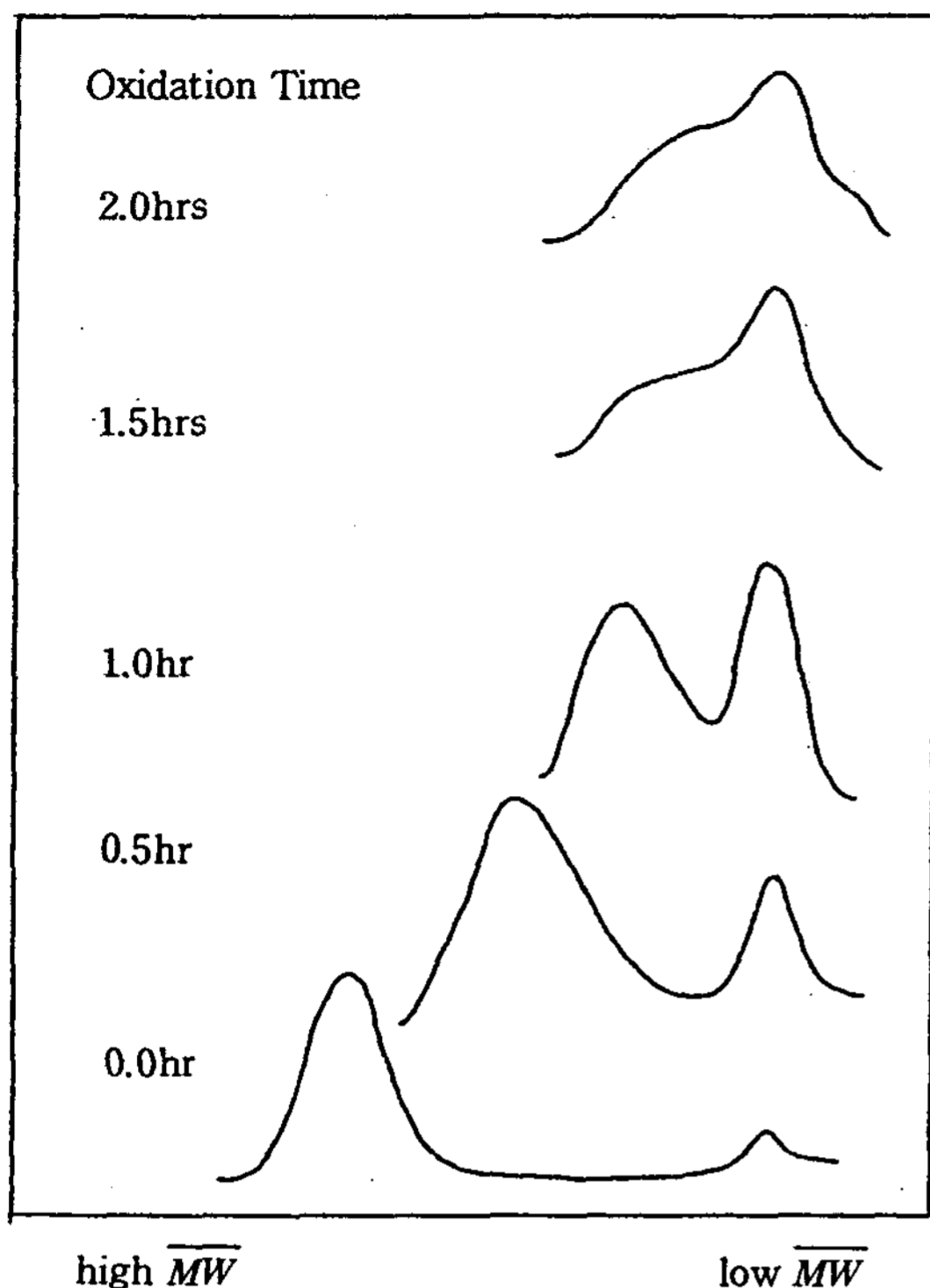


Fig. 4. GPC chromatograms of the extracts from LMPS/PVME = 35/65 oxidized at 110°C.

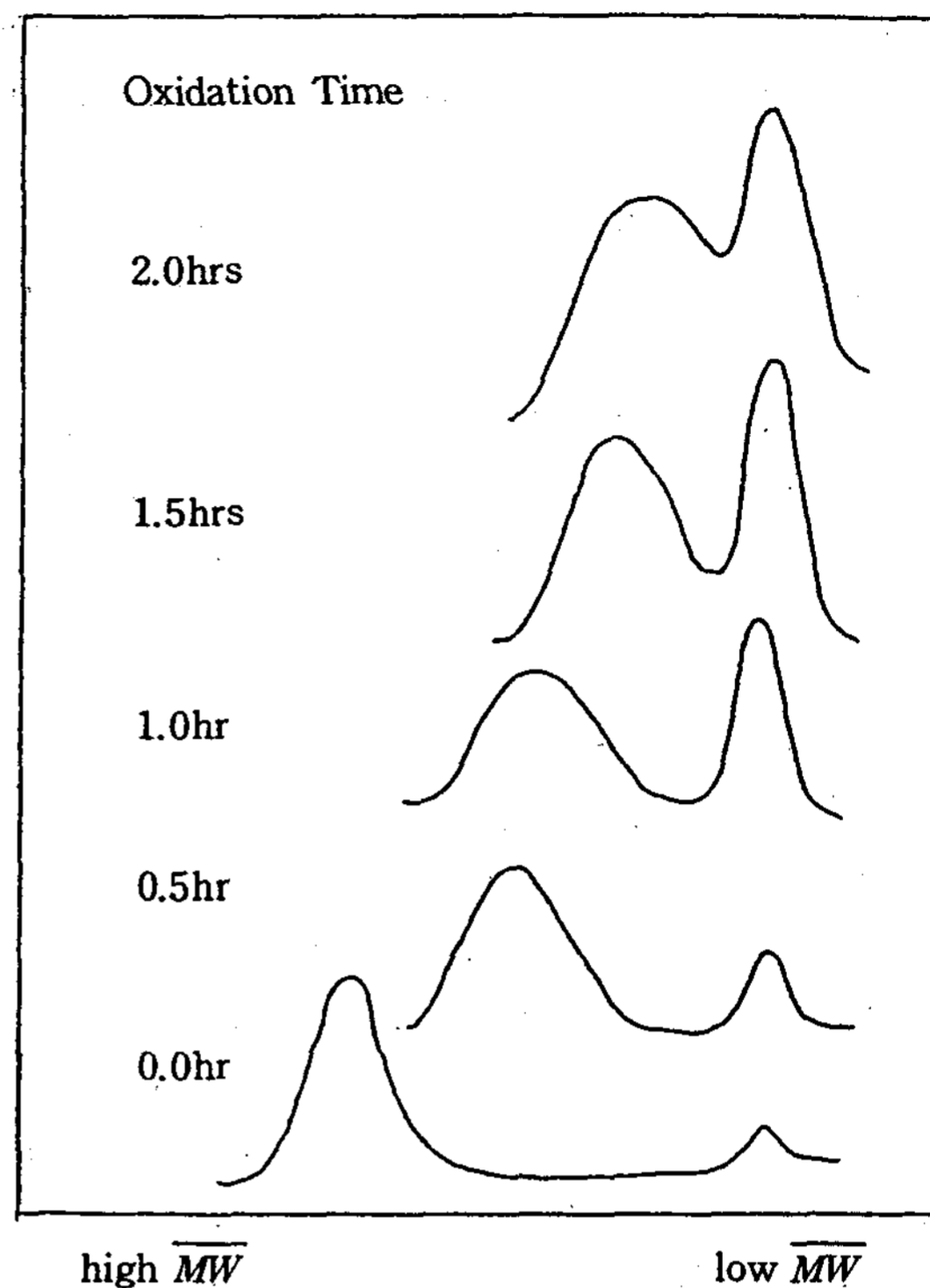


Fig. 5. GPC chromatograms of the extracts from LMPS/PVME = 50/50 oxidized at 110°C.

the low molecular weight portion of added PS. As oxidation time increased, the PVME peak moved to low molecular weight side, and overlapped with the low molecular weight PS peak. Besides the peak height of low molecular weight PS increased. Similar patterns were observed for LMPS/PVME = 50/50 and 65/35 (Figure 5, and 6). As the amount of the added PS increased the severe overlap between two peaks did not occur. From the molecular weight decreasing trend, the peak which changed its position was the peak of the oxidized PVME. The molecular weight change of PVME are given in Figure 7. The molecular weight of PVME decreased more slowly in the blends as PS content increased. Compared with decrease of molecular weight of PVME in high molecular weight PS/PVME, the decrease

of molecular weight of PVME in LMPS/PVME was slower.¹⁵⁾ The other peak which did not change the peak position corresponded to $\bar{M}_n = 1,600$. To elucidate the nature of the PS in the extract from the oxidized blends, another separation method was employed. First of all, PVME in methanol was separated by using the previously mentioned method. After drying the methanol completely water was added to the dried film. Immediately a small amount of white precipitate was obtained. Figure 8 shows the UV spectra of PVME and PS. The separated PS from the extract showed the same UV spectra as PS (Figure 9). The possibility of oxidized PS and bonding to PVME could be excluded because GPC chromatogram showed two separated peak originally and all extracts gave PS precipitates

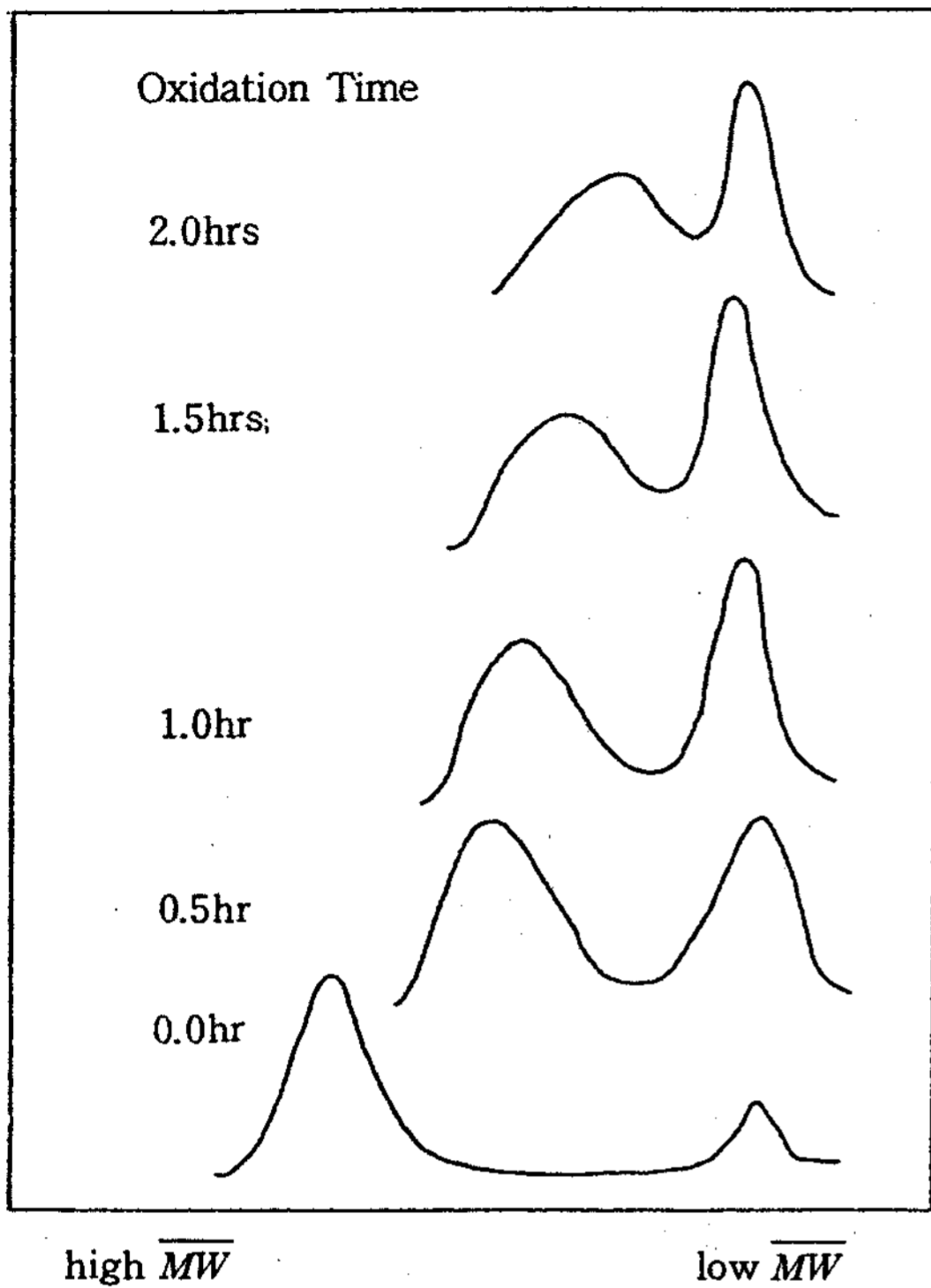


Fig. 6. GPC chromatograms of the extracts from LMPS/PVME = 65/35 oxidized at 110°C.

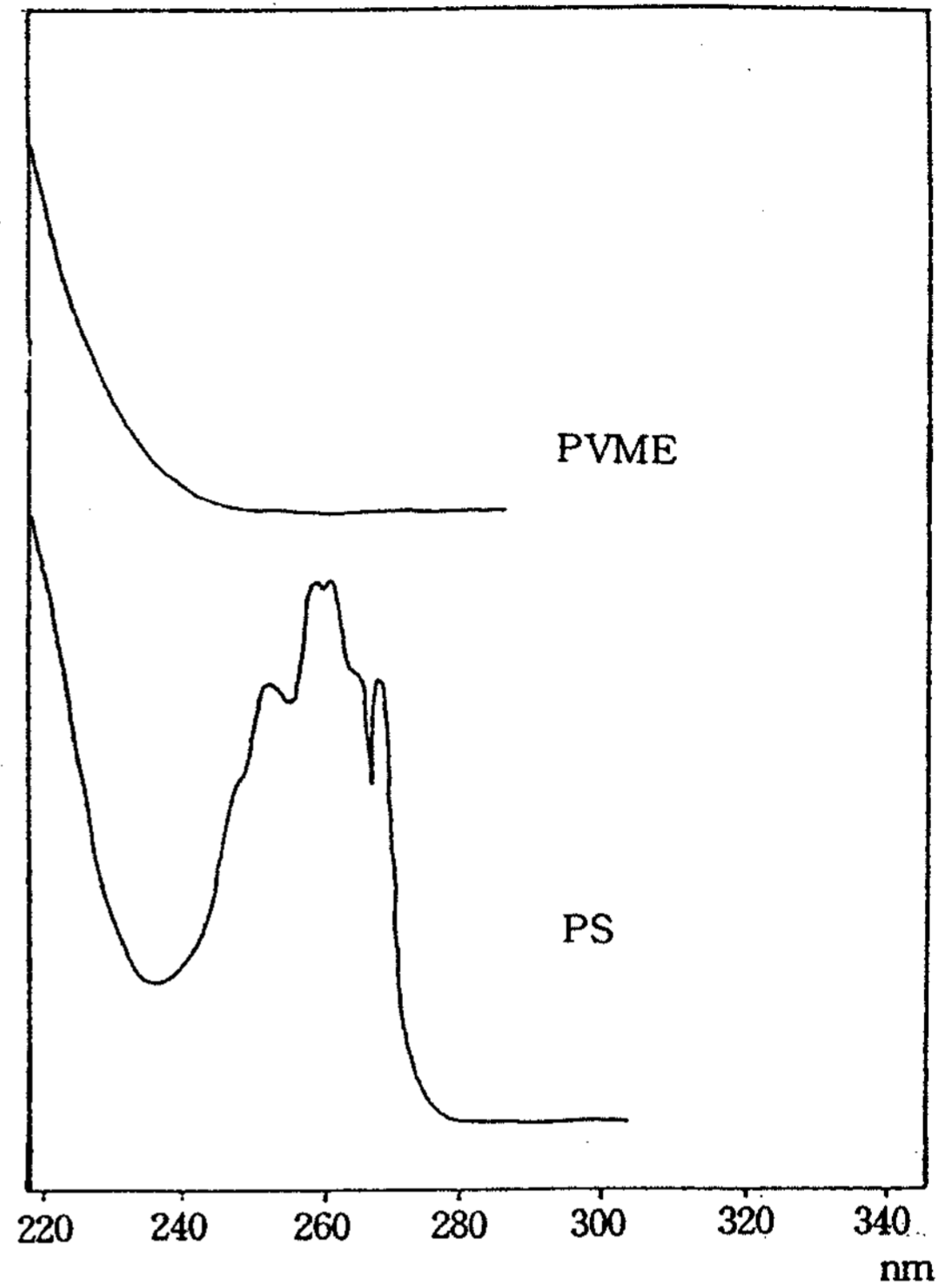


Fig. 8. The UV spectra of PVME and PS.

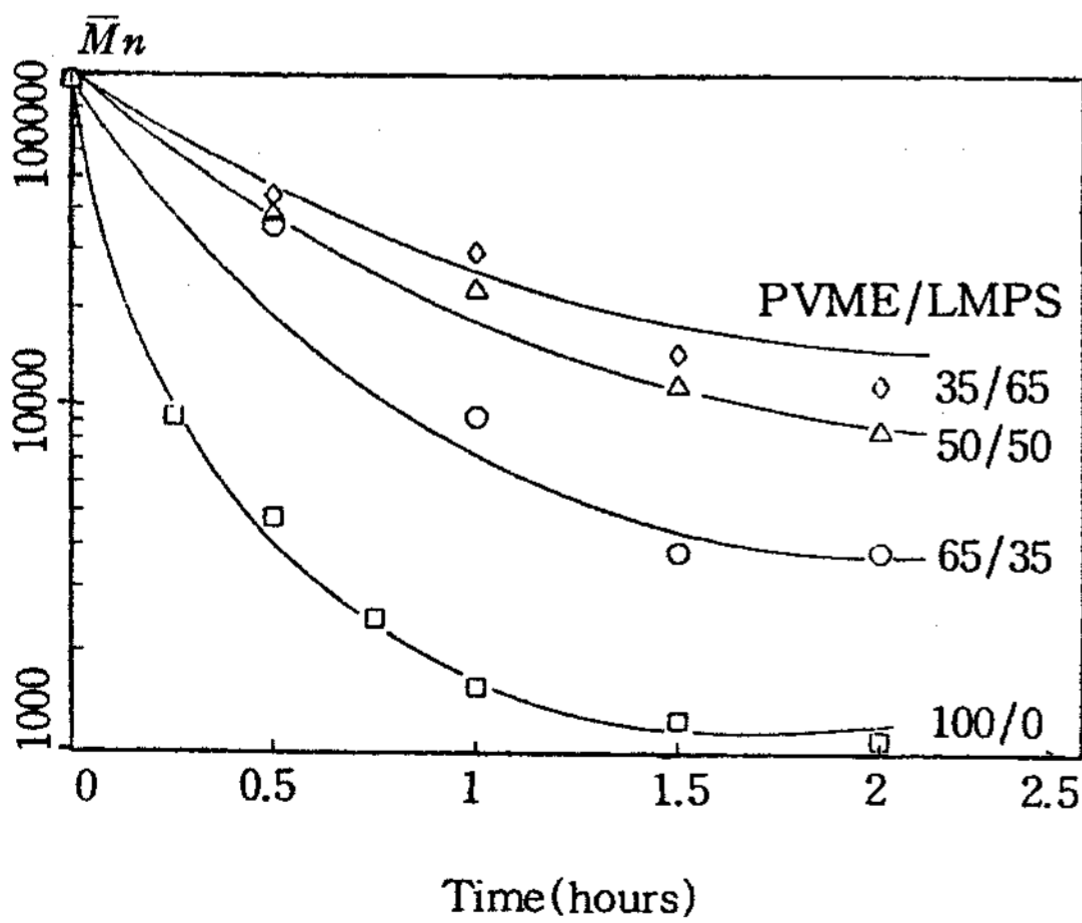


Fig. 7. Number average molecular weight changes of PVME from LMPS/PVME blend after oxidation at 110°C.

from water solution. It was concluded that during the sample separation the low molecular weight portion of the original PS was dissolved in methanol due to its low molecular weight. The precipitated PS in water solution did not change their molecular weight (Figure 10). The FT-IR spectra of the precipitated PS are given in Figure 11. The chemical structure of precipitated PS does not change throughout the oxidation.

2, 4-Diphenylpentane was synthesized as a model compound of LMPS (Figure 12). It is organic crystalline material. This compound was mixed with PVME. Figure 13 shows oxidation curves of 1, 5, and 10% of the model compound which was added to PVME at 110°C. It showed a little lengthening of the induction periods. The oxidation rates were nearly same as that of PVME (Figure 13). The molecular weight chan-

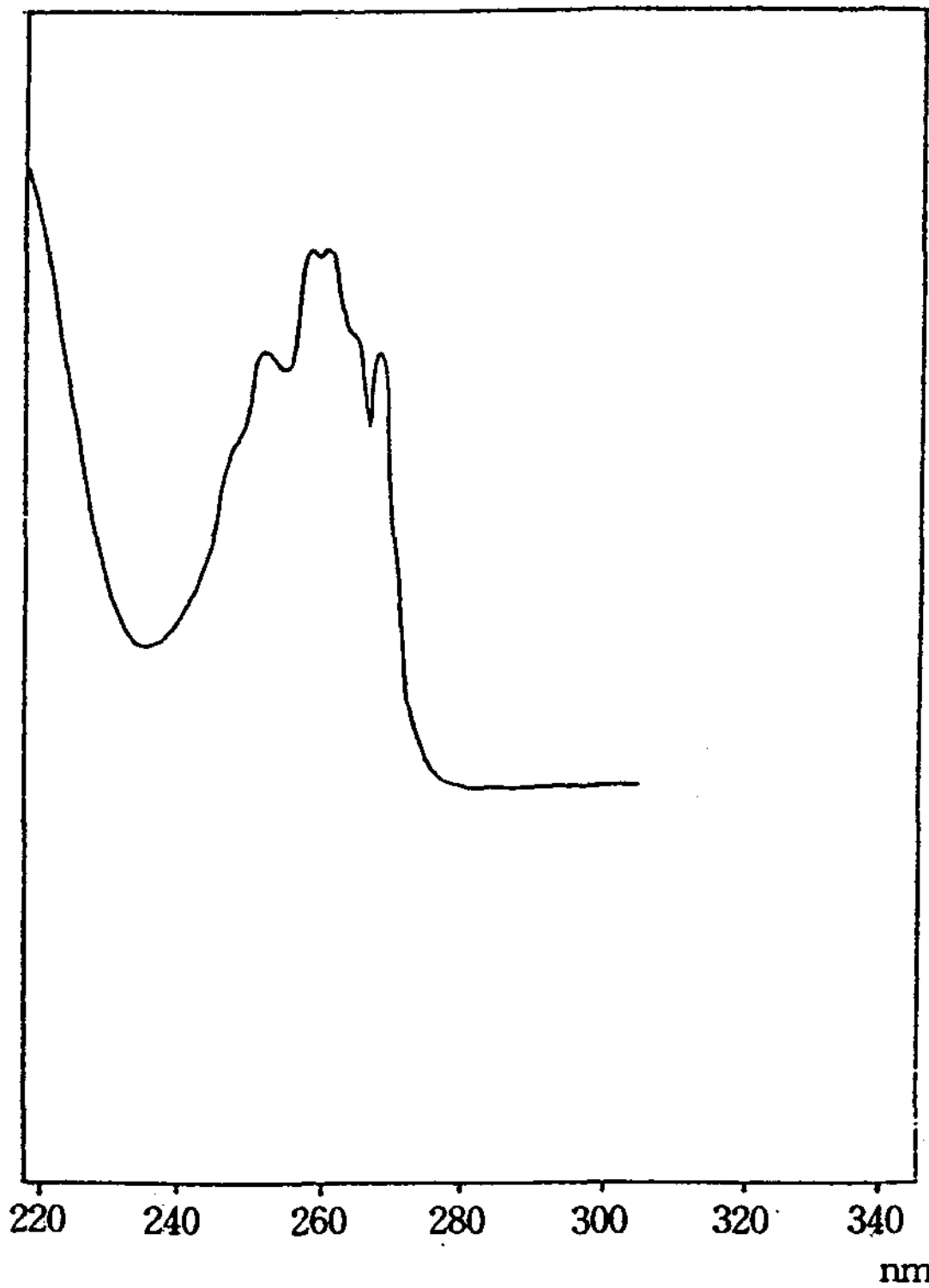


Fig. 9. The UV spectra of PS separated from extract of LMPS/PVME = 50/50 blend oxidized at 110°C.

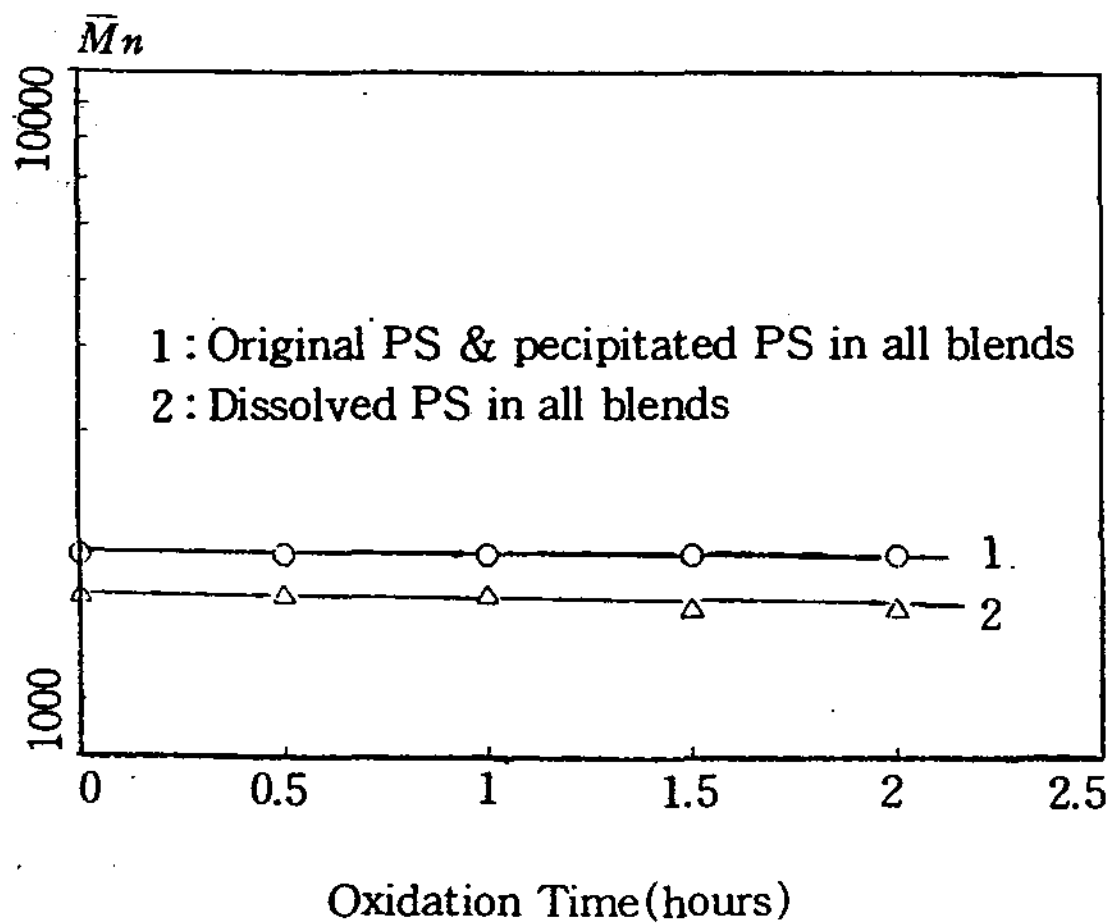


Fig. 10. Number average molecular weight changes of PS and PS separated from LMPS/PVME blend and dissolved PS in all blends.

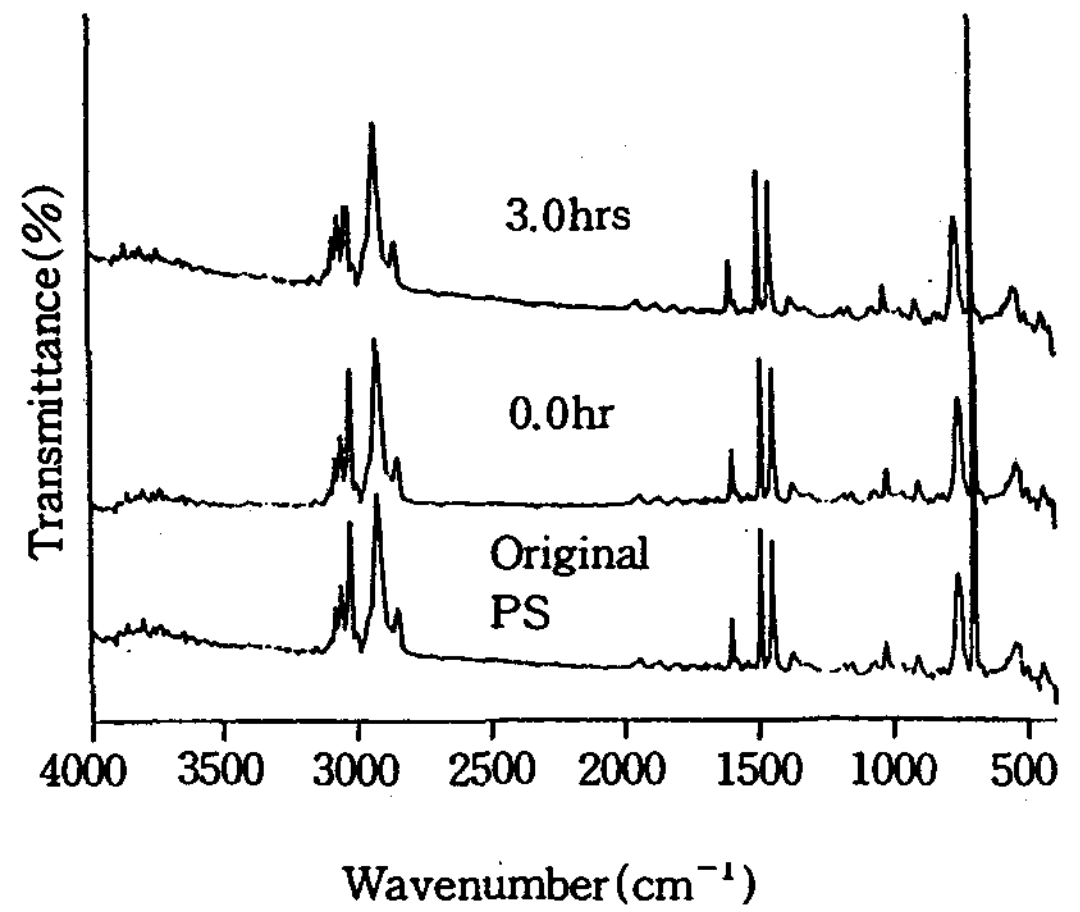


Fig. 11. FT-IR spectra of original PS and PS separated from LMPS/PVME = 50/50 blend oxidized at 110°C.

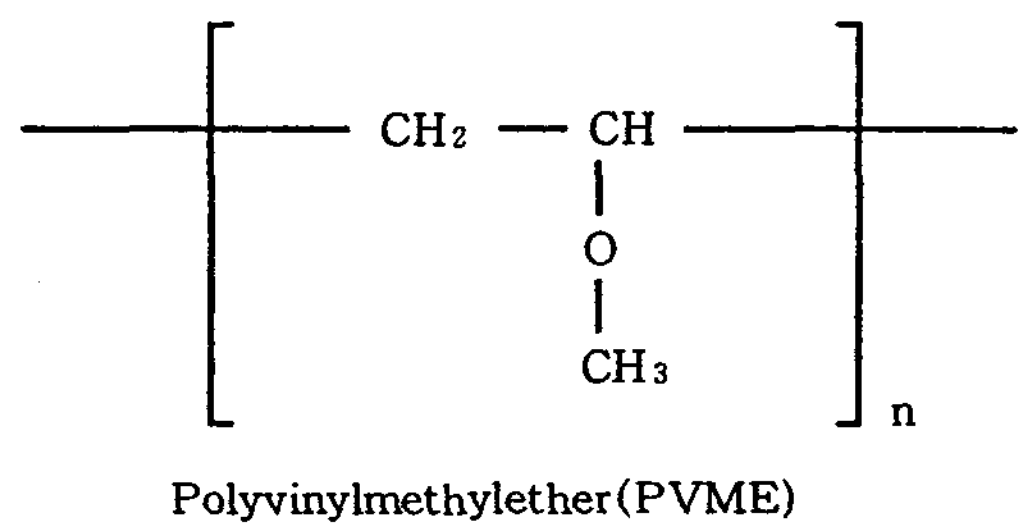
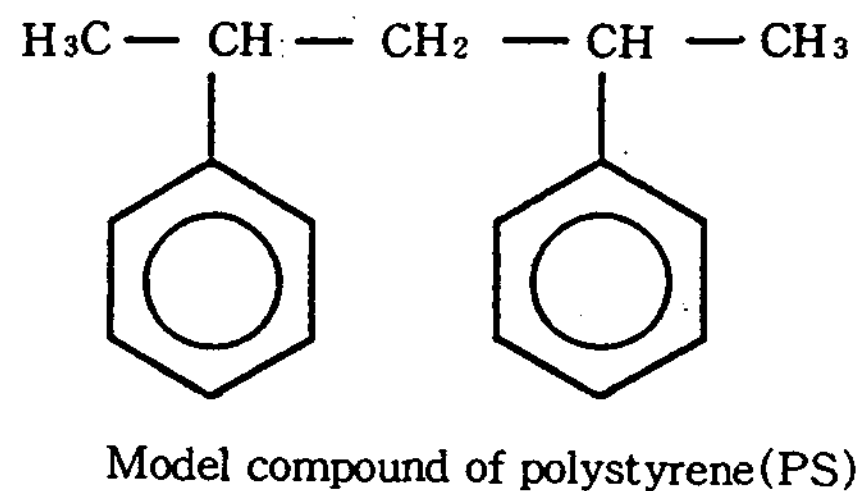


Fig. 12. The chemical structure of model compound of PS and PVME.

ges of PVME are given in Figure 14. It showed a little enhancement of the molecular weight decrease. If the amount of the model compound increased up to 10%, the mixture showed crystalline domains, and did not give a uniform film. Even though the model compound appeared to

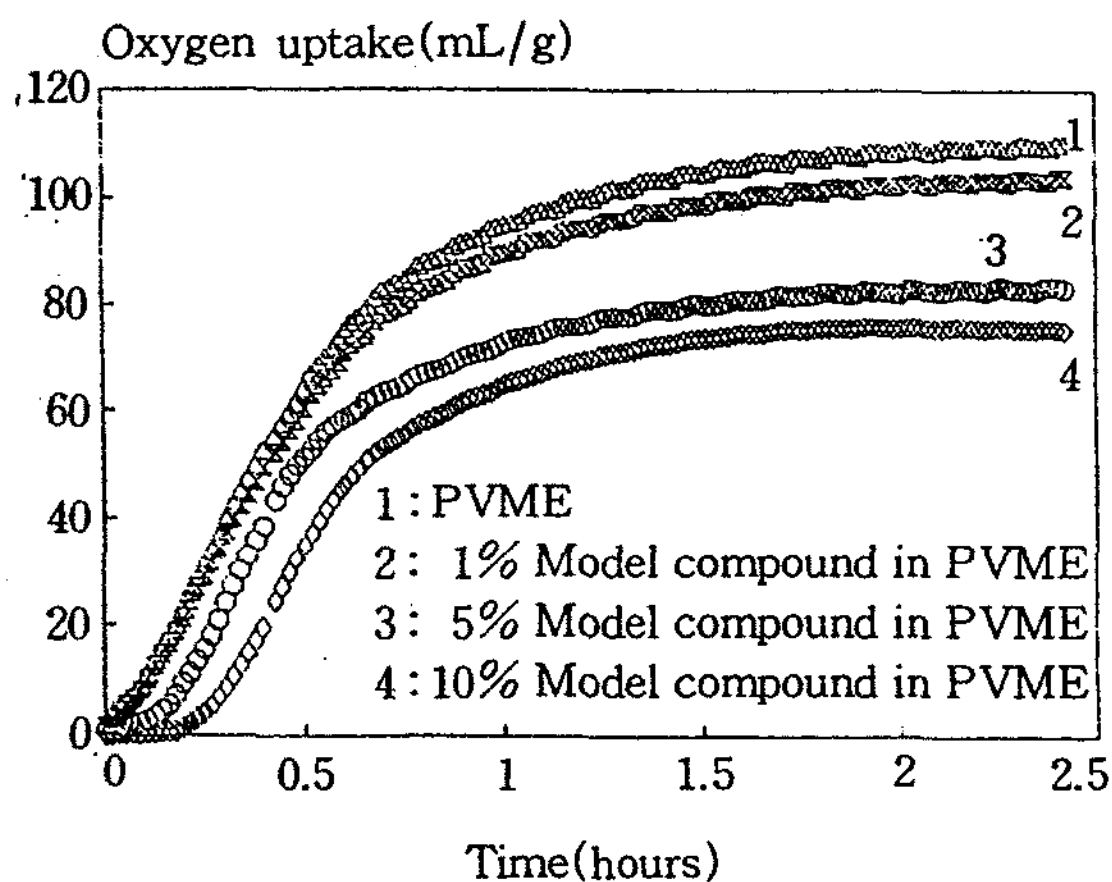


Fig. 13. Oxygen absorption of model compound of PS and PVME.

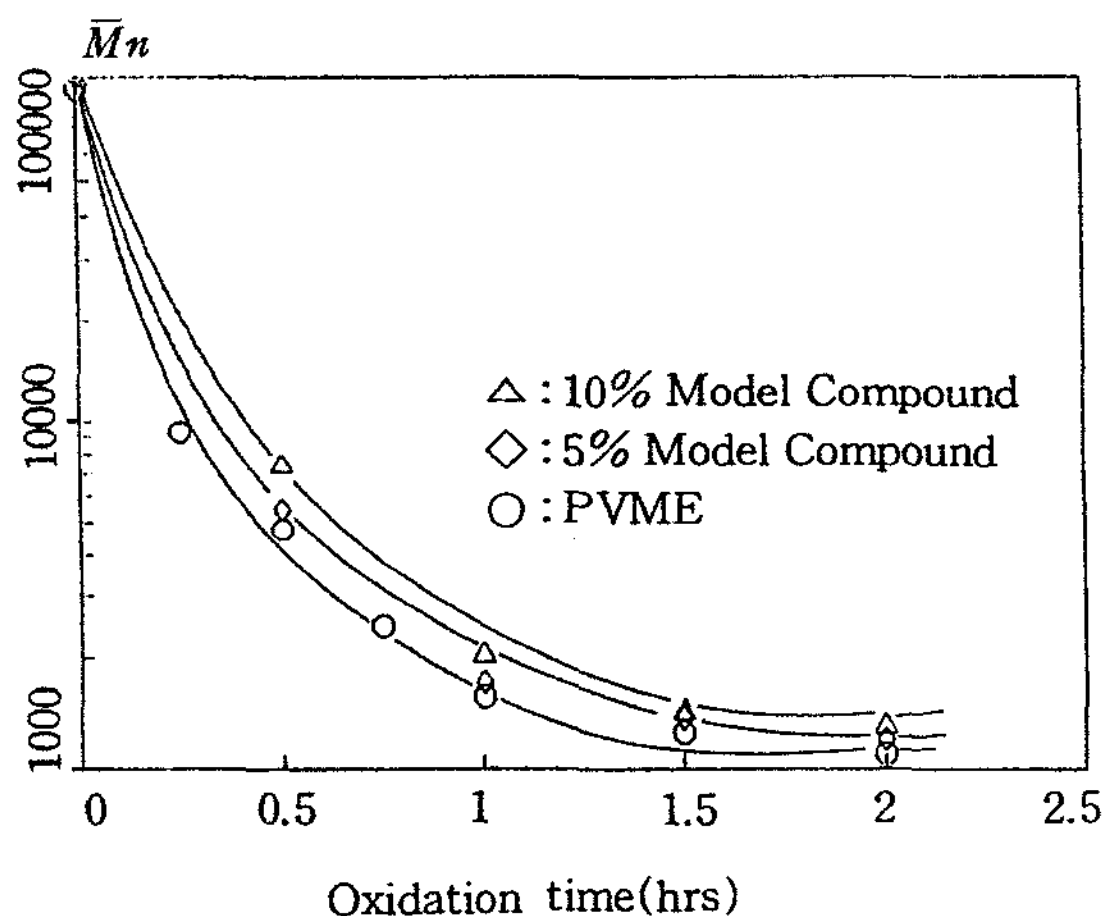


Fig. 14. Number average molecular weight changes of separated PVME from model compound of PS and PVME oxidized at 110°C.

form clear and uniform film below 10% of the model compound, they did not a significant retardation effect on oxidation of PVME.

IV. Conclusion

The molecular weight of PVME in low molecular weight PS/PVME decreased more slowly

than that of PVME in high molecular weight PS/PVME. The molecular weight of PS did not change during the oxidation. When the constituents of the oxidized blend were separated, low molecular weight portion of PS and the oxidized PVME were dissolved together in methanol, 2, 4-Diphenylpentane was synthesized as a model compound for LMPS. The mixture of 1, 5, and 10% of the model compound and PVME were oxidized. The model compound did not show a retardation effect on the oxidation of PVME.

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