저 분자량 Poly(styrene)과 Poly(vinylmethylether) Blend의 열 산화에 대한 연구 I

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

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요 약

저 분자량(M_w=1970)의 poly(styrene)(PS)와 poly(vinylmethylether)(PVME)의 블렌드를 열 산화시킬 때 저 분자량의 PS의 첨가량이 증가할수록 유도기간이 증가하며 열 산화 속도는 감소함을 알 수 있었다. 열 산화 과정 동안 저 분자량 PS와 PVME 블렌드는 상 분리를 보이지 않았다. 저 분자량을 갖는 PS와 PVME 블렌드에서 PVME의 산화 속도는 높은 분자량을 갖는 PS와 PVME 블렌드에서 PVME의 열 산화 속도보다 훨씬 느려짐을 보였다.

Introduction

The mixture of poly(styrene) (PS) and poly(vinylmethylether) (PVME) was one of the most extensively studied blends[1~10] and their structures are shown in Figure 1.
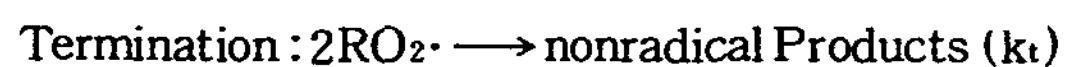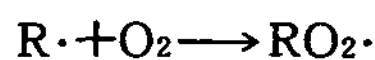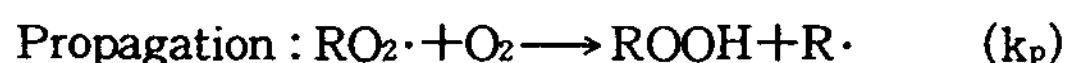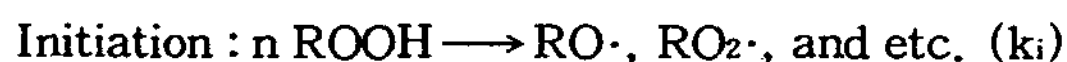
They formed miscible blends through the whole range of compositions when they were cast from the aromatic hydrocarbon solvents such as toluene and benzene but gave the opaque and heterogeneous blends from chlorinated solvents such as trichloroethylene or methylene chloride. The miscible blends showed typical lower critical solution temperature (LCST) behavior and thermal induced phase separation is reversible.[3,4] The interaction parameter between PS and PVME was determined by several different methods to be negative indicative of favorable mixing.[5~7] The interaction between the phenyl group of PS and the ether group of PVME was proposed to be the main driving force for the miscibility through deutrated PS experiments.[8,9] PVME has 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 sus-

ceptible 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 reactants and heat as the energy source has been a major factor in polymer degradation.

Polystyrene 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.[11]

In recognition of the autocatalysis of the oxidation by hydroperoxide, the process was commonly referred to as autoxidation. Autoxidation showed the characteristic S-shaped curve for oxygen absorption as a function of time, that is, the reaction began to increase slowly in rate as the hydroperoxide product contributed to the ever-increasing rate of initiation until a maximum rate was obtained, and then the reaction subsided and leveled off as the polymer became modified by oxidation(Figure 2). Autoxidation, defined as the thermal oxidation that take place between room temperature and about 200°C, proceeded by a typical free radical chain mechanism. The following kinetic scheme has been proposed to explain the autoxidation of hydrocarbon polymer.[12]

Initiation : $n\ ROOH \longrightarrow RO\cdot, RO_2\cdot$, and etc. (k_i)

Propagation : $RO_2\cdot + O_2 \longrightarrow ROOH + R\cdot$ $\quad(k_p)$

$\qquad\qquad R\cdot + O_2 \longrightarrow RO_2\cdot$

Termination : $2RO_2\cdot \longrightarrow$ nonradical Products (k_t)

$\qquad\qquad 2R\cdot \longrightarrow R\text{-}R \qquad\qquad (k_t{'})$

$\qquad\qquad RO_2\cdot + R \longrightarrow RO_2R \qquad (k_t{''})$

First, chemical bonds in the polymer were broken to form radicals as the initial products. These reactive radicals were relatively short-lived and reacted rapidly with other available reactants.

Chain scission occurred only when bonds of the backbone chain were broken chain were broken irreversibly. Because of the restricted motion in a polymer matrix, recombination of radicals could
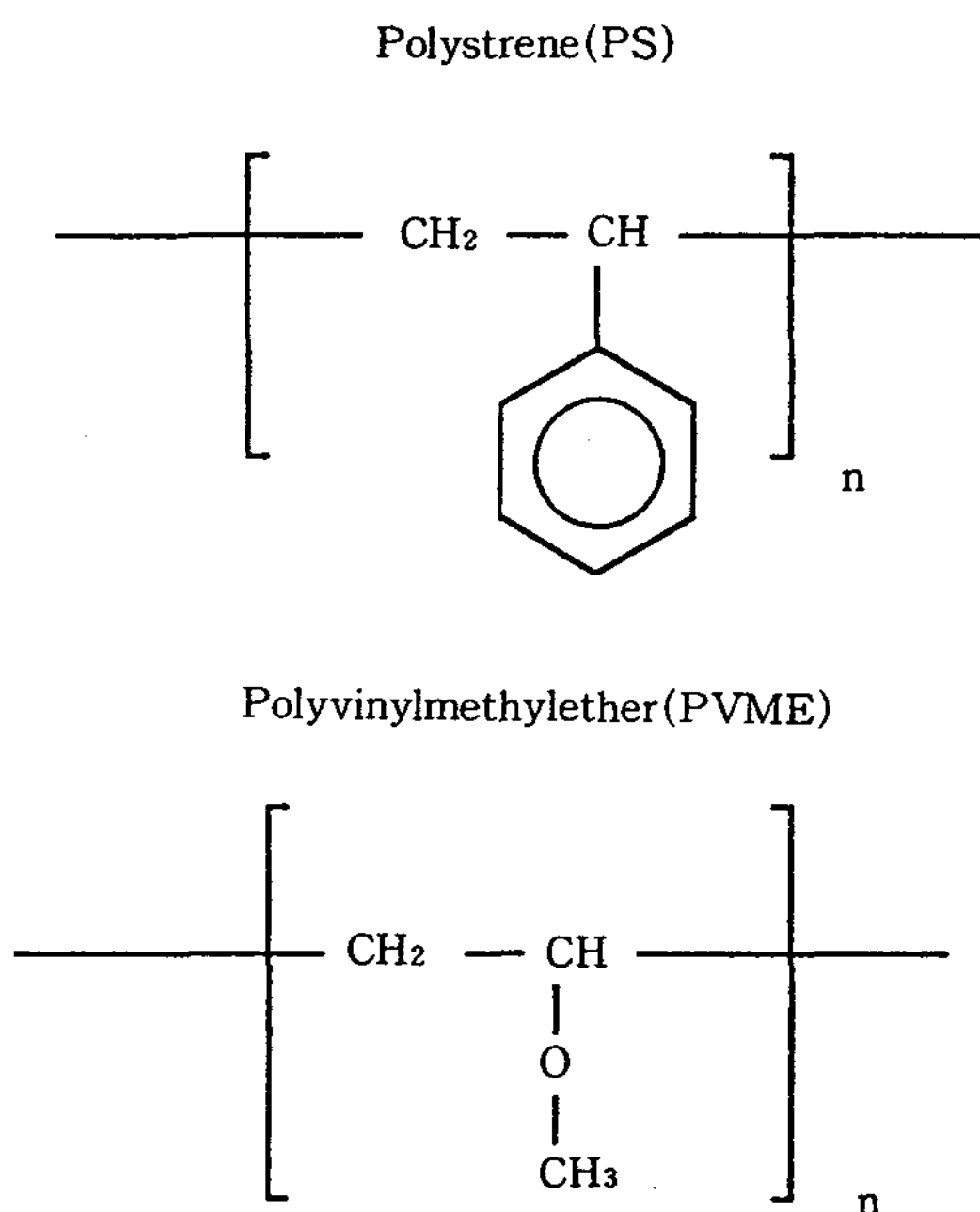
Polystrene(PS)

Polyvinylmethylether(PVME)

Fig. 1. The chemical strcture of polystyrene and polyvinylmethylether.
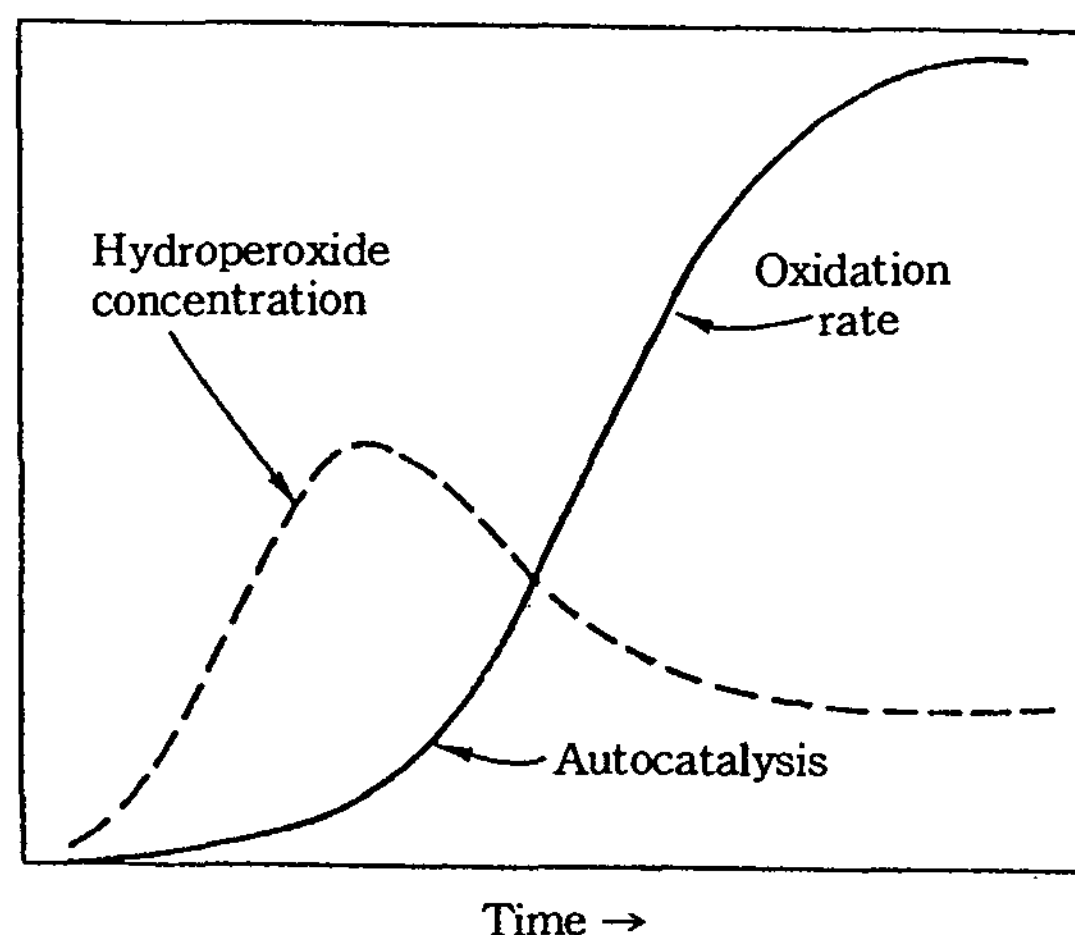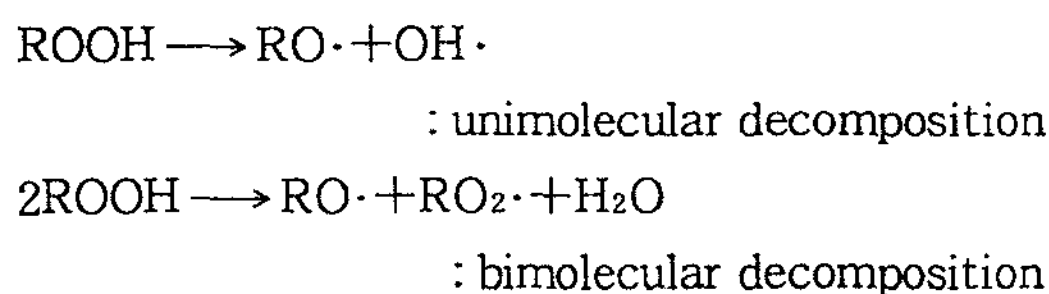

Fig. 2. Relationship between hydroperoxide decomposition and the role of oxidation.

occur to reverse the process of chain scission. Minute traces of hydroperoxides could be present initially. Peroxides and other oxygenated compounds incorporated into a polymer during its synthesis or processing may increase its susceptibility to oxygen. Both first and second-order decomposition[13] of the hydroperoxide have been observed in the autoxidation of simple compounds in the liquid phase, with the bimolecular process becoming dominant as the concentration of hydroperoxide reached critical value. Under this condition the hydroperoxide groups were close enough to associate each other.

$$ROOH \longrightarrow RO \cdot + OH \cdot$$
$$: \text{unimolecular decomposition}$$
$$2ROOH \longrightarrow RO \cdot + RO_2 \cdot + H_2O$$
$$: \text{bimolecular decomposition}$$

In the early stages of autoxidation, the random introduction of hydroperoxide at a isolated site in the polymer would be expected to favor unimolecular decomposition.

Propagation was a chain reaction in which a single initiation event could lead further reaction in hundreds of other molecules. Chain reactions of propagation and oxidative chain branching were responsible for the rapid degradation that occurred during autoxidation. As the hydroperoxides accumulated, the rate of branching increased, and this led to autocatalytic stage. The maximum hydroperoxide concentration was reached at that point where hydroperoxide decomposition exceeded its rate of formation, and this coincided with the rapid increase in reaction rate. If a steady-state concentration of $RO_2 \cdot$ was attained, the rate of initiation, R_i could be set equal to the rate of termination, R_t, and solved for the steady-state concentration $[RO_2 \cdot]$

$$R_i = R_t = 2k_t [RO_2 \cdot]_2$$
$$[RO_2 \cdot] = \{R_i/2k_t\}^{0.5}$$

Hydrogen atom abstraction by peroxy radical from the substrate was the rate determining step in the oxidation of polymers. The rate of oxidation (R_{ox}) could be derived by substitution of the steady-state radical concentration in the expression for the rate-determining propagation reaction :

$$R_{ox} = k_p[RO_2][RH]$$
$$= k_p(R_i/2k_t)^{0.5}[RH]$$

Thus the rate of uninhibited autoxidation could be expected to be independent of oxygen concentration in the case of pure materials, provided there is no significant limitation upon the availability of oxygen attributable to the the concentration or to rate of diffusion.[12] The situation was quite different, however, if oxidizable impurities were present or if stabilizers against thermal oxidation were added. The present work was an extension of the earlier study[14, 15] to the oxidation behavior when the molecular weight of poly (styrene) was reduced to $M_w = 1970$.

Experimental

1. Materials

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 120000 and the polydispersity was 1.26. Styrene monomer was obtained from Aldrich Co. The inhibitor in styrene was removed by an inhibitor removal column(Polysciences 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 pur-

ified styrene was obtained from a middle portion of distillate from vacuum distillation.

2. Polymerization of low molecular weight monodispersed PS

Low molecular weight polystyrene was synthesized by anionic polymerization using sec-butyllithium(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 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℃, a precalculated amount of sec-butyllithium was injected. The polymerization was terminated after 2 hours by adding a small amount of methanol. Polystyrene was recovered and purified by toluene and methanol. The molecular weight of purified PS was confirmed by GPC. The M_w and polydispersity were 1970 and 1.07, respectively.

3. Preparation of polymer blends

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

4. Oxygen uptake measurement

The oxygen uptake measurement apparatus is shown in Figure 3. The amount of consumed oxygen was measured by monitoring the pressure change in a constant volume oxidation cell. Cal-

cium oxide(Aldrich Chemical Co., 99.95% purity) was placed in the cell to absorb the evolved gases. Pyrex glass wool which was preoxidized at 150℃ 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/RC-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 N_2 gas and placed in the heating block for 10 minutes. After 15 minutes of vacuum procedure, pure O_2 gas was introduced into the cells and an initial pressure of 770 mmHg 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.

5. Differential Scanning Calorimetry (DSC)

A Dupont 9900 thermal analyzer connected with a Dupont 910 differential scanning calorimeter was used for the glass transition temperature(T_g) measurements. DSC samples were prepared by cutting the solvent-cast films into proper sizes. The sample weight was 10 mg. Samples for DSC analysis were scanned at 10℃/min from -50℃ to 100℃, then cooled at cooled at 10℃/min.

Results and Discussion

Anionically polymerized poly(styrene) having a molecular weight of 1970 and polydispersity of 1.
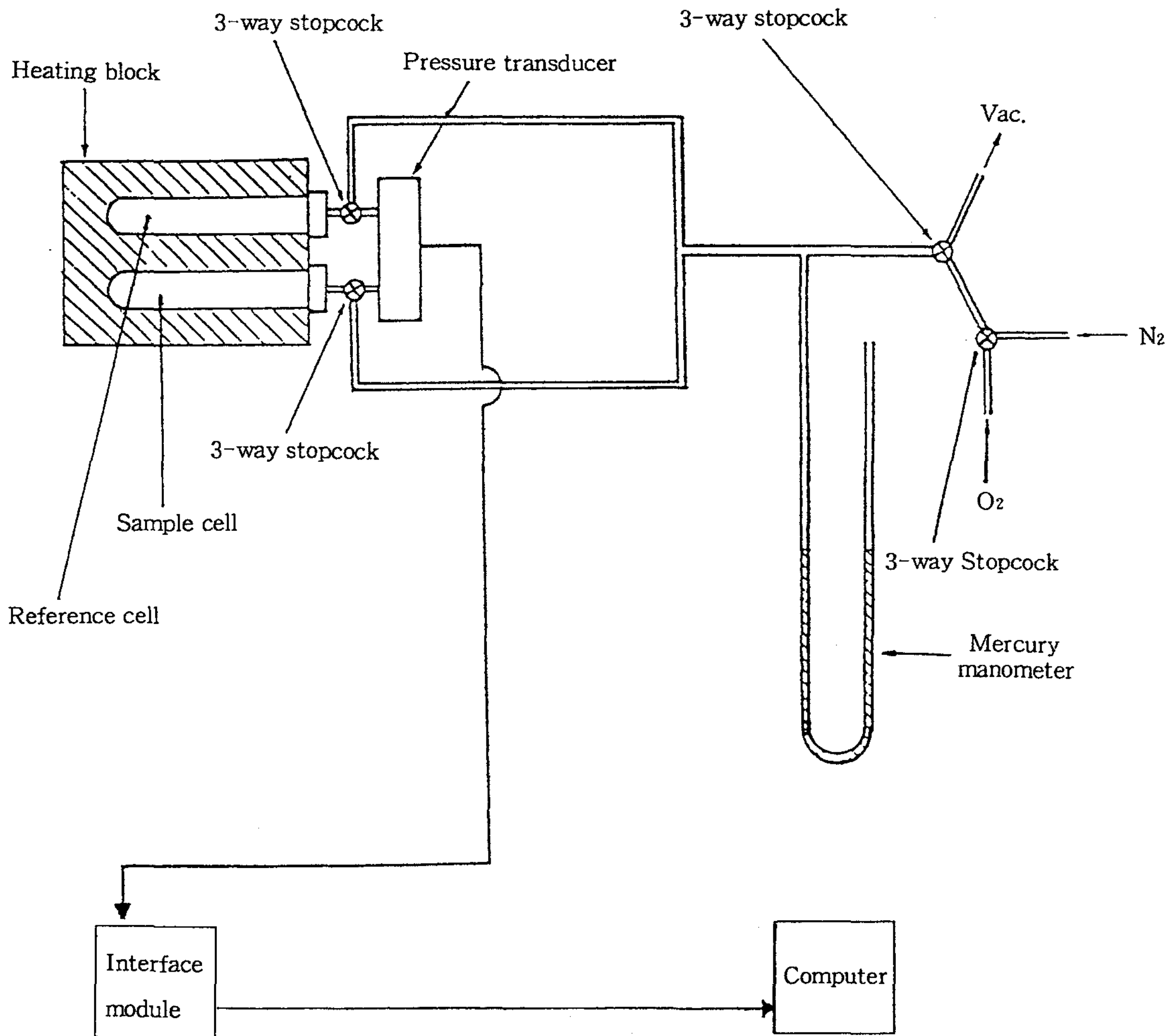
Fig. 3. Schematic diagram of oxygen uptake measurement set-up for thermal oxidation.

07 was used. Low molecular weight poly(styrene) (LMPS), poly(vinylmethylether)(PVME), and three blends [LMPS/PVME=65/35, LMPS/PVME=50/50, and LMPS/PVME=35/65] were oxidized under a pure oxygen atmosphere at C and 140°C. To measure and compare the true oxidation rates, we needed to ascertain that the film thickness was appropriate so that the oxidation rate was not limited by the rate of dif-fusion of oxygen into polymer matrix. Figure 4 shows the glass transition temperature of LMPS/PVME blends.

Oxidation rate was obtained from the slope of the steady state region, and the induction period is defined as the time at which steady state line extrapolates to zero absorption. After the steady state region, the oxidation curve began to deceler-ate, and this is believed to be due to the deple-
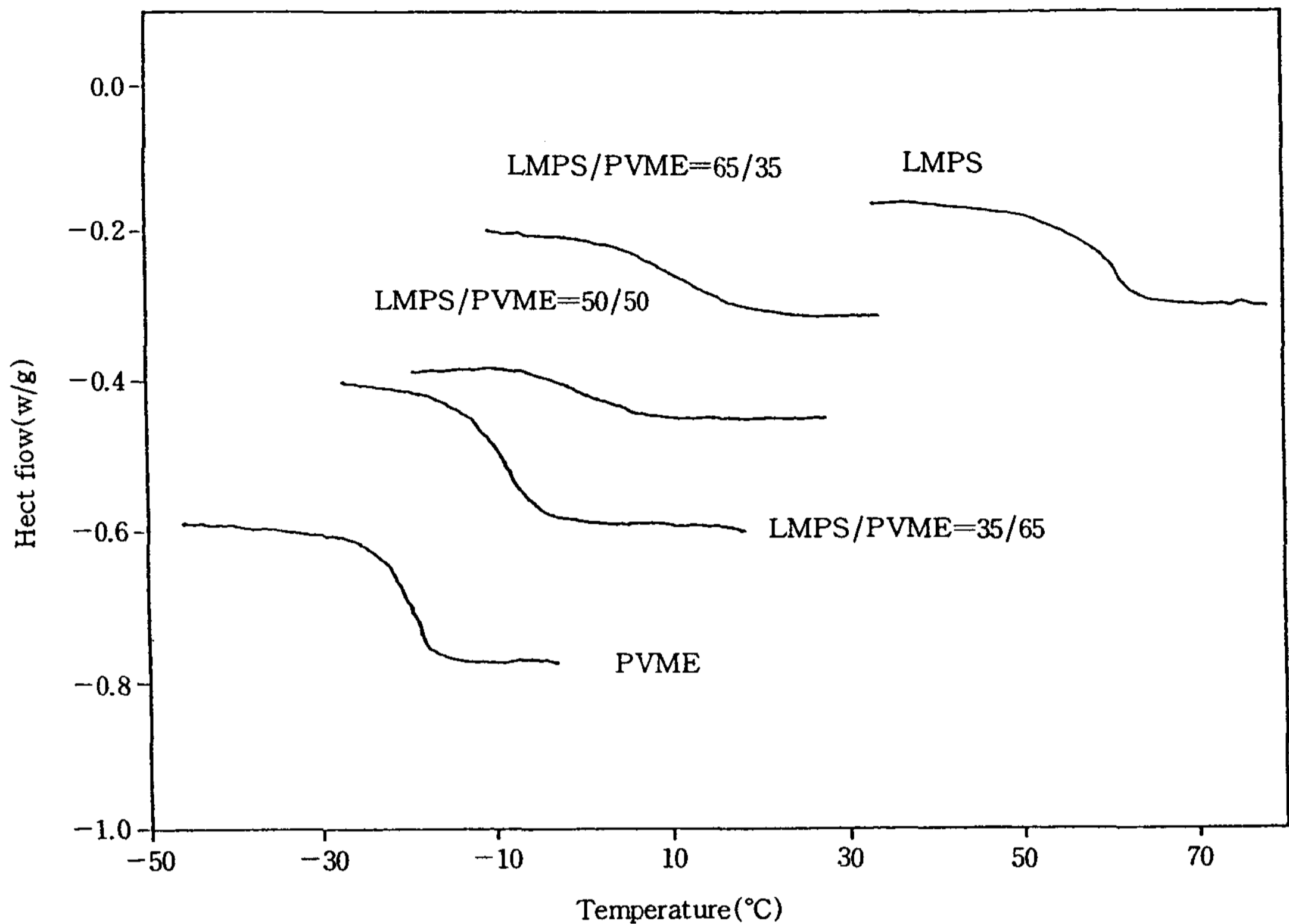
Fig. 4. Glass transition temperature of LMPS/PVME blends measured by DSC.

tion of accessible materials.

Figure 5 and 6 show the oxidation curves of LMPS/PVME at 110°C and 140°C. As expected, PVME was oxidized very rapidly, and PS showed no measured oxidation within the experimental time. PS has been reported to have an introduction period of longer than 10000 hours at 110°C. Since PVME was readily susceptible to oxidation, subtle changes in the sample preparation procedure caused large fluctuations in oxygen uptake time. To minimize the data fluctuation, all sets of samples were prepared at the same time from the purification to storage.

During the oxidation of these blends at 110°C and 140°C, they didn't show phase transition, in contrast to high molecular weight of PS(HMPS)

/PVME blend. This occurred because the cloud point curves of PS/PVME blends move to markedly higher temperatures when the molecular weight of PS was decreased.[14, 15] For example, the use of low molecular weight PS, prepared by anionic polymerization to have a M_w of 2300 and M_w/M_n ratio of 1.1, elevated the phase separation temperature to well above the degradation temperature of PVME.

At 110°C and 140°C, each blend had a different induction period and oxidation rate. After the deceleration of oxygen absorption, the oxygen uptake curves reached plateau regions. The oxidation rate were not proportional to the PVME content in the blends unlike HMPS/PVME(Figure 7 and 8). The oxidation rates and induction periods at
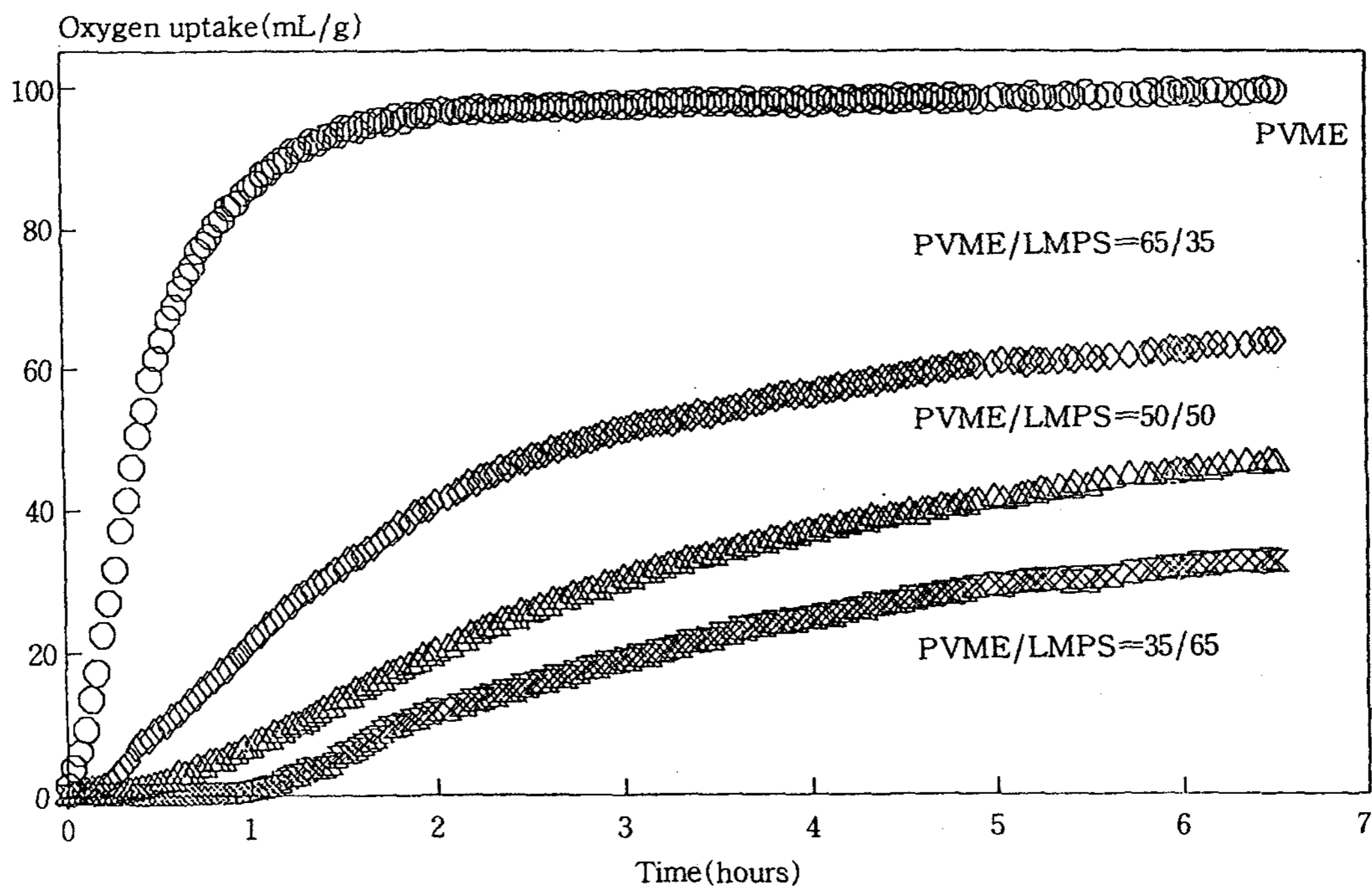
Oxygen uptake(mL/g)

PVME

PVME/LMPS=65/35

PVME/LMPS=50/50

PVME/LMPS=35/65

Time(hours)

Fig. 5. Oxygen absorption of LMPS/PVME blends at 110℃.

Oxygen uptake(mL/g)

PVME

PVME/LMPS=65/35

PVME/LMPS=50/50

PVME/LMPS=35/65

Time(hours)
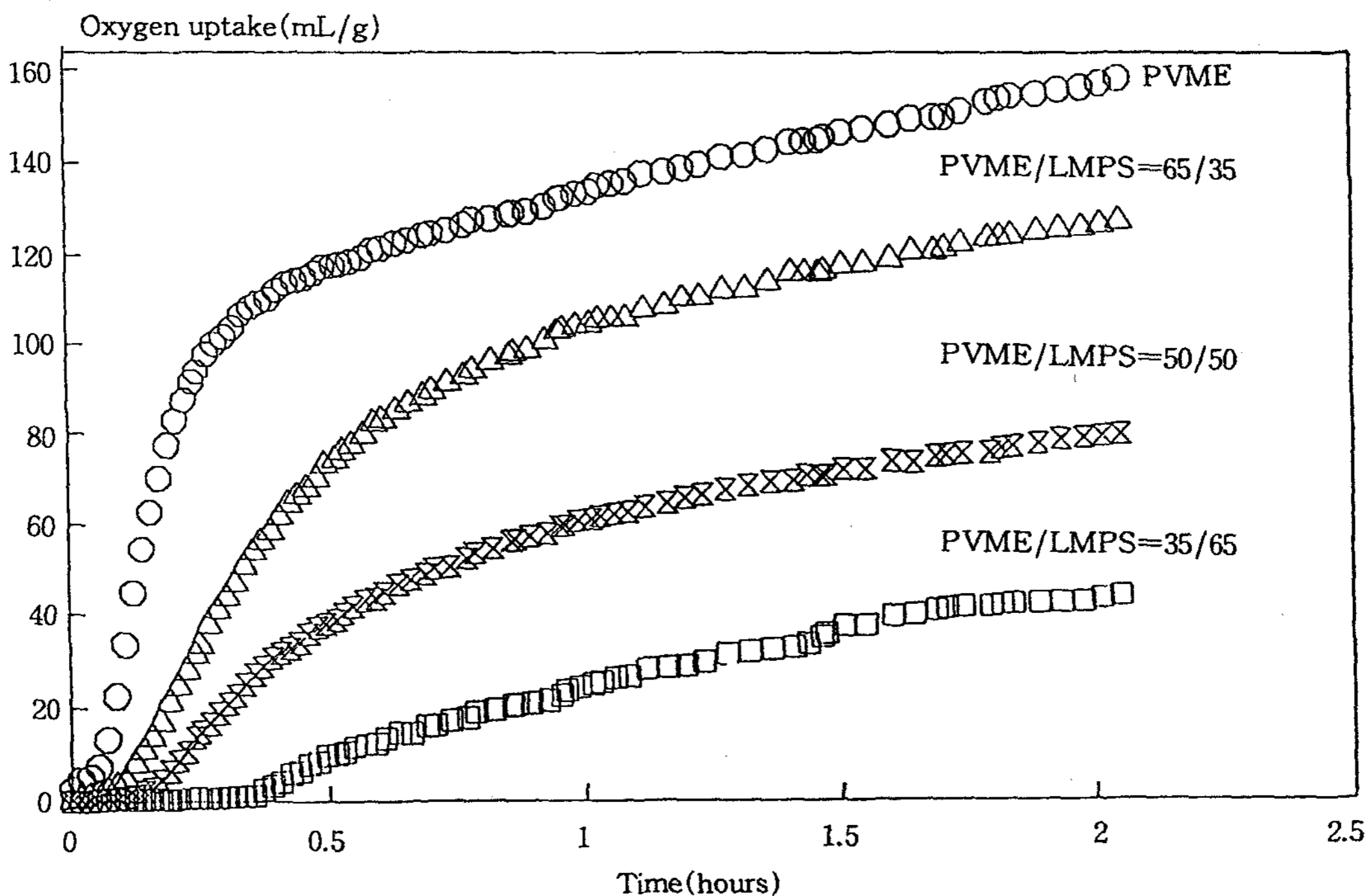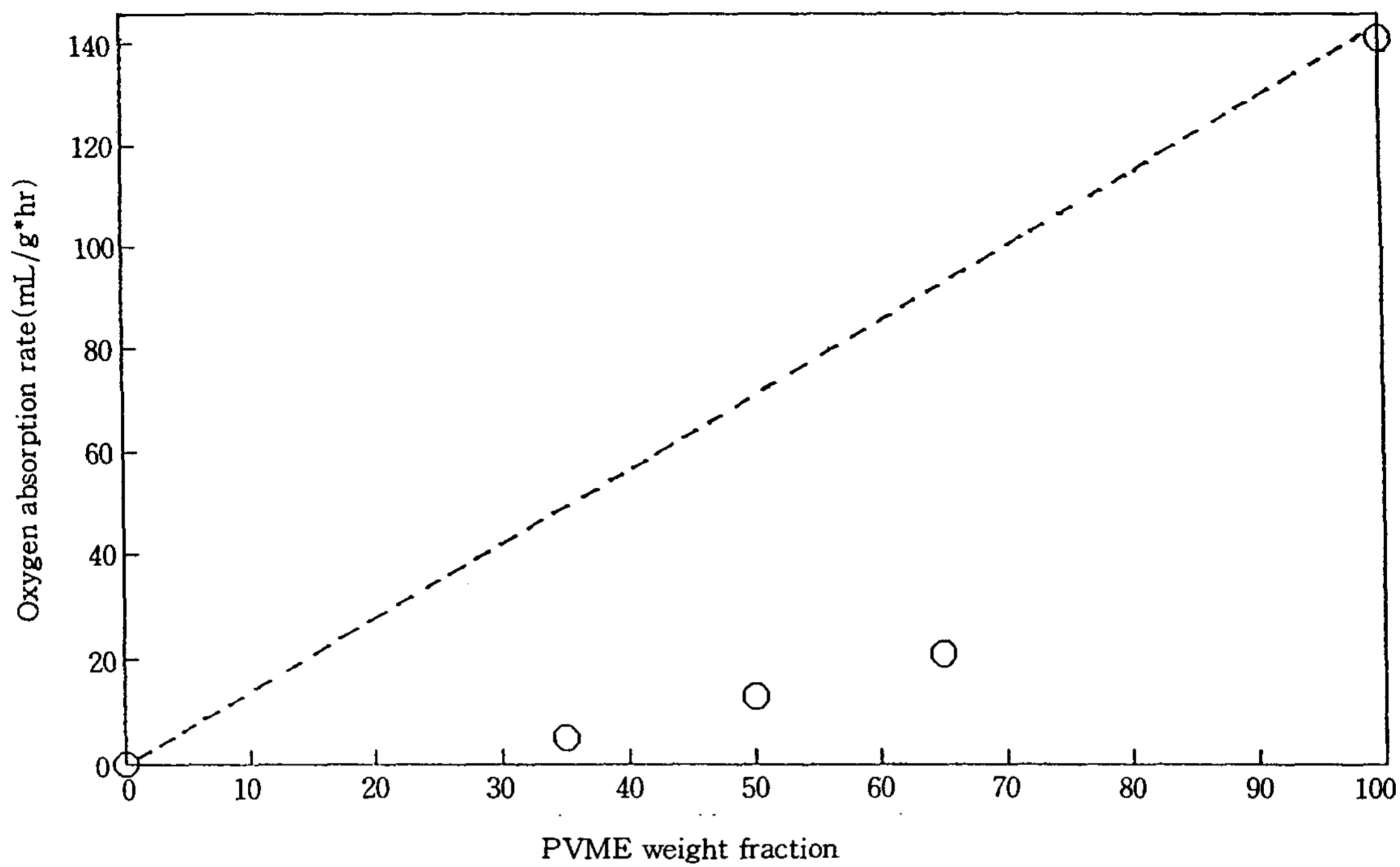
Fig. 6. Oxygen absorption of LMPS/PVME blends at 140℃.
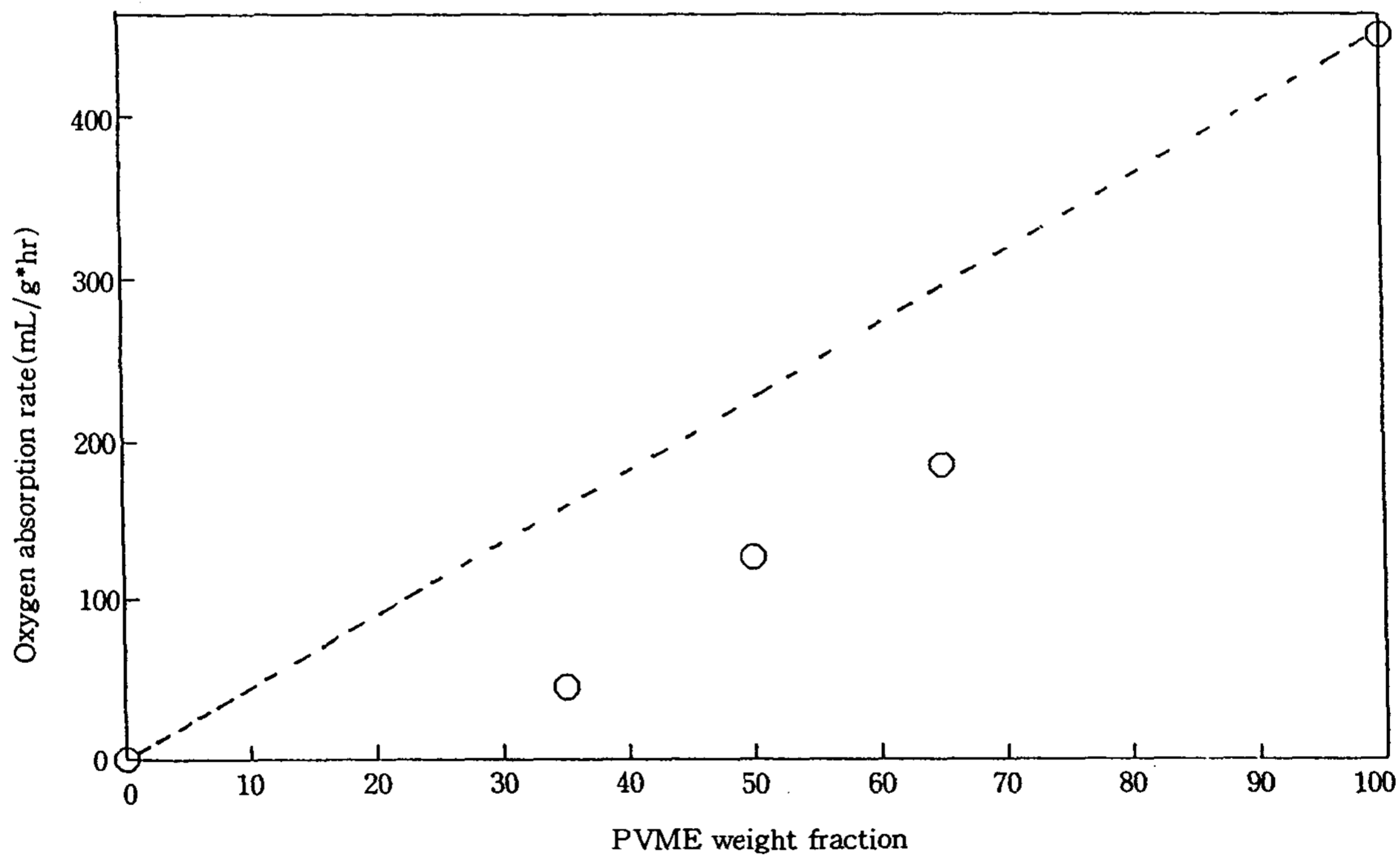
Fig. 7. Oxygen absorption of LMPS/PVME blends at 110℃.

Fig. 8. Oxygen absorption rate of LMPS/PVME blends at 140℃.

110℃ and 140℃ are shown in Table 1.

The spectra of PVME showed a broad absorption peak at 3200~3500 cm^{-1} which is ascribed to the absorption of hydroxyl and hydroperoxide groups. In addition, a peak appeared at 1740 cm^{-1} which represented the absorption of several different carbonyl groups and primary esters (Figure 9). The observed decrease in tertiary C-H

Table 1. Induction periods and oxidation rates of LMPS/PVME blends at different temperature

Experiment temperature	Blend	Induction period(min)	Oxidation rate(mL/g·hr)
110℃	PVME	2	140.7
	LMPS/PVME=35/65	7	21.1
	LMPS/PVME=50/50	13	13.2
	LMPS/PVME=65/35	25	5.1
140℃	PVME	5	448.1
	LMPS/PVME=35/65	20	184.3
	LMPS/PVME=50/50	40	126.2
	LMPS/PVME=65/35	75	45.1

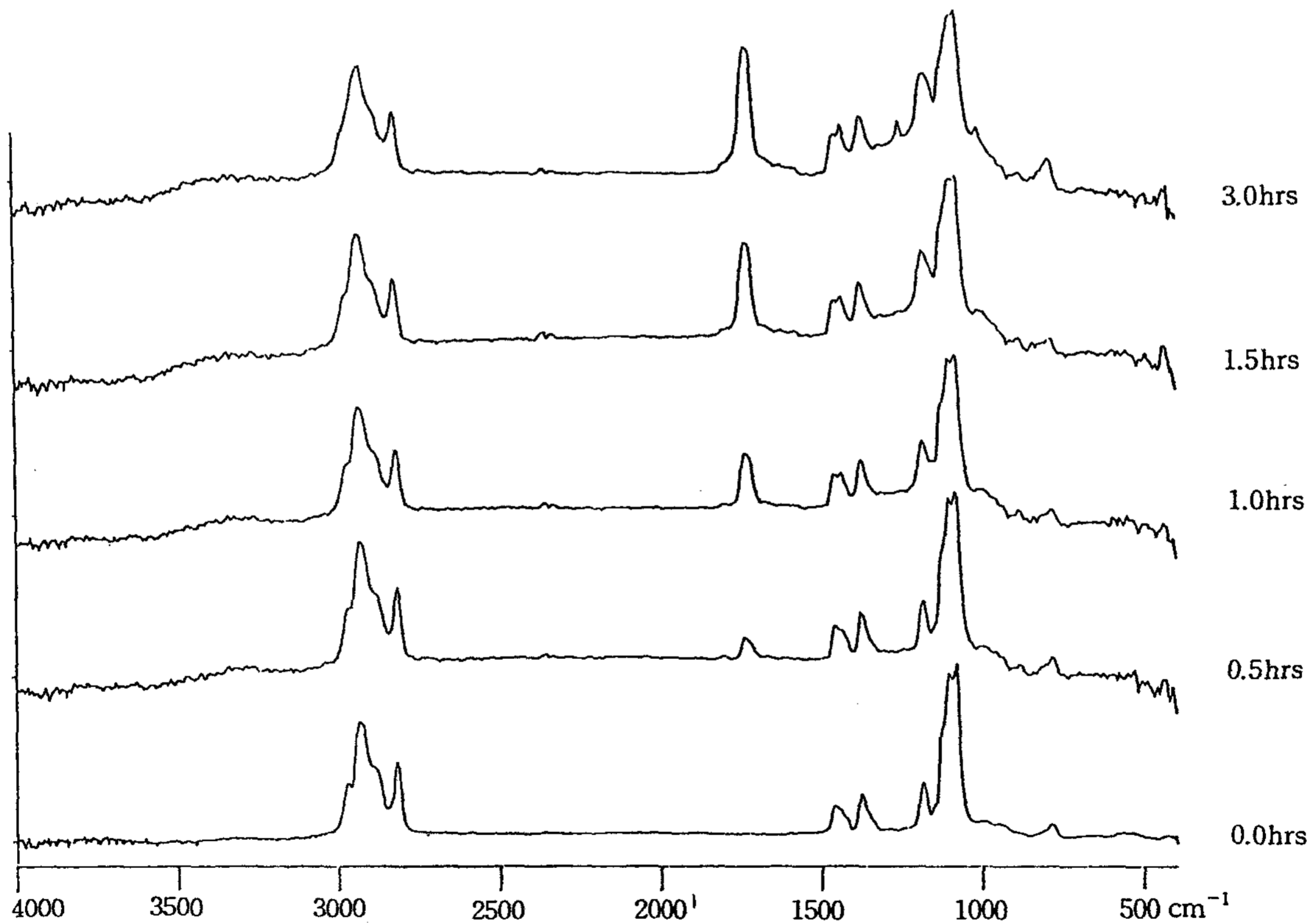Fig. 9. FT-IR spectra of PVME oxidized at 110℃.

groups at 2980 cm^{-1} indicated that the tertiary hydrogen was a major site of oxygen attack after oxidation. Since the tertiary hydrogen of PVME could be easily abstracted, subsequent reactions involving hydroperoxide formation and decomposition followed by β-scission for the alkoxy radical provided a reasonable path to ester formation. The probable sequence of these reactions are given in Figure 10.

To investigate the chemical structure of the oxidized PVME separated from the oxidized blen-

ds, the sample separation was attempted by using a precipitation method. The PVME in the oxidized blend was filtered by using 0.4m 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.

Conclusion

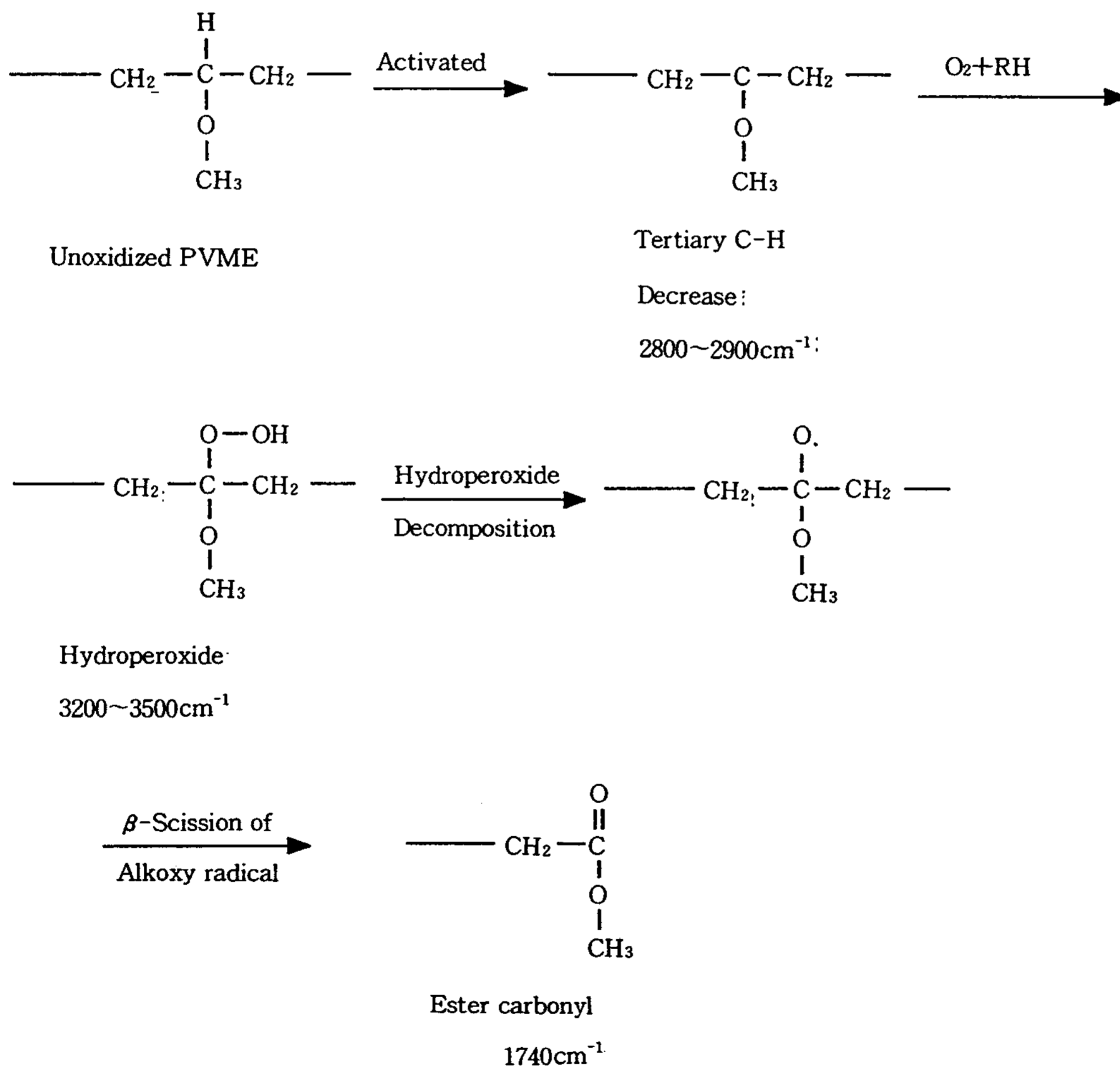The thermal oxidation of polymer blends, par-

Fig. 10. The schematic sequence of oxidation of PVME.

ticularly low molecular weight poly(styrene)(PS) and poly(vinylmethylether)(PVME), was studied systematically. Since PVME was easily oxidized, while PS was not, PVME underwent chemical structure changes such as the formation of carbonyl groups and hydroxyl groups, as well as chain scission during the oxidation. Generally speaking the induction periods became longer upon adding more PS to the PVME. Their oxidation rates were less than the simple mathematical sum of each component's and the overall activation energies for oxidation were raised.

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