$\overline{M_n}$ values of the resulting insoluble polymers, which were higher with 1 mol % catalyst than with 3 mol % catalyst.

Considerable lowering of the initiation temperature by introduction of α-methyl (**2b**) and *p*-methoxy (**2c**) substituents seems to be attributable to the high efficiency of the initiation step of the polymerization with **2b** or **2c**. This is because both the structure of the propagating species and the rate of the polymerization (k_p) are expected to be the same in these three cases, and, therefore, the concentration of the cationic species liberated by heating **2b** or **2c** (via S_N1 or S_N2 process) should be much higher than that from **2a**. In fact, benzylic carbocations formed from **2b** and **2c** are strongly stabilized by the inductive and resonance effects of their substituents, and hence both **2b** and **2c** generate the cationic species even at a lower temperature than that for **2a**.

On the other hand, the fact that maximum conversion (ca. 65%) with 1 mol % catalyst is less than that with 3 mol % catalyst (ca. 90%) would indicate the occurrence of some termination reactions. One termination mechanism might be reaction of the propagating oxonium salts with liberated *p*-cyanopyridine to form the very stable pyridinium salt which is no longer an effective catalyst.

Thus, activation-aided modification of a benzyl group of **2a** resulted in the synthesis of **2b** and **2c** with highly enhanced catalytic activities and good thermal latency in comparison with **2a**. This catalyst activation by introduction of a cation-stabilizing group is in good accord with the results of the substituent effects observed in the polymerization of a bicyclo ortho ester with substituted benzyl sulfonium salts reported by Endo et al.[4a]

In conclusion, we have synthesized new pyridinium salts as highly activated latent thermal catalysts, (*p*-methoxybenzyl)- (**2c**) and (α-methylbenzyl)-*p*-cyanopyridinium hexafluoroantimonates (**2b**). These are stable, soluble in monomer, easy to handle, and show much higher catalytic activities than benzyl-*p*-cyanopyridinium hexafluoroantimonate (**2a**) in the cationic polymerization of glycidyl phenyl ether (**1**) as a model cationically polymerizable monomer.

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Registry No. 1 (homopolymer), 25265-27-4; 1 (SRU), 100629-24-1; **2a**, 116146-28-2; **2b**, 124156-72-5; **2c**, 123173-67-1; benzyl chloride, 100-44-7; *p*-cyanopyridine, 100-48-1; α-methylbenzyl bromide, 585-71-7; *p*-methoxybenzyl chloride, 824-94-2.

Thermal Oxidation of Blends of Polystyrene and Poly(vinyl methyl ether)

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ABSTRACT: Thermal oxidation of blends of polystyrene and poly(vinyl methyl ether) was studied at 80, 110, and 140 °C. The oxygen uptake by PS was negligible, but PVME oxidized rapidly. The induction period of 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 the 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 reaction between PVME radicals and PS took place during the induction period to result in less reactive PS radicals. When low-molecular-weight polystyrene was blended with PVME, the mixtures remained homogeneous throughout the oxidation reaction. The induction periods became longer and oxidation rates slower than the values for the corresponding PS blends.

I. Introduction

Although polymer blends have become an important class of materials, our knowledge of their chemical stability is inadequate. There is scattered information in the literature about thermal degradation of heterogeneous blends[1] and thermal or photo oxidation of rubber-modified polystyrene.[2-4] But the oxidation of miscible polymer blends has received only occasional attention.[5]

In the study of oxidation of mixtures of small molecules, Russell found that the rates of oxidation were not additive.[6,7] A decrease in the rate of oxidation to below the value for either component was observed when a small amount of the more easily oxidized tetralin was added to cumene. It was concluded that tetralyperoxy radical terminated much more readily than cumylperoxy radical, and a lower rate of oxidation of the mixture resulted from the lowered steady-state concentration of peroxy radicals. The purpose of the present investigation is to study whether the oxidative rates of miscible blends obey the additivity rule. Departure from the additive rule would suggest cross-propagation or cross-termination reactions in the blend. By cross-propagation, we mean the reaction of oxy or peroxy radical A with polymer B to form

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an inactive species A and a radical of polymer B that in turn reacts with oxygen. In cross-termination reactions, two dissimilar radicals react to form nonradical products.[6,7] The crossover reactions should also manifest themselves in chemical and molecular weight changes. Our investigation therefore centered on the measurement of (1) oxygen uptakes of the blends and (2) molecular weight and chemical changes of the component polymers.

The blend of our choice consists of polystyrene (PS) and poly(vinyl methyl ether) (PVME). The two polymers are chosen for several reasons: (a) The rates of thermal oxidation of the two polymers differ by a factor of at least 100[5], with PVME being the more reactive polymer. (b) The two polymers are known to be miscible over the entire range of compositions.[8,9] (c) The glass transition temperature of PS is 106 °C and that of PVME, −30 °C. Therefore, thermal oxidation experiments can be conducted at moderate temperatures that are nevertheless higher than the T_g values of the blends. (d) Miscible blends of the two polymers undergo phase separation when heated to temperatures above ≈120 °C. Thus, it is possible to measure oxidation rates of a blend in both the miscible and the immiscible states. The results can provide useful insight into the dependence of oxidation rate on the degree of segmental mixing as it relates to the crossover reactions mentioned above.

II. Experimental Section

(1) Materials. Poly(vinyl methyl ether) was obtained from Aldrich Chemical Co. and purified by precipitating twice from 7 to 10% (w/v) toluene solution into an excess of hexane. It was dried in a vacuum oven at room temperature for 3 days. The number-average molecular weight of PVME was determined by gel permeation chromatography (GPC) to be 66 000 (PS equivalent).

Polystyrene was synthesized in the laboratory by radical polymerization in bulk using azobis(isobutyronitrile) (1.8×10^{-4} g/g) as initiator at 70 °C for 12 h. The polymer was purified by precipitation into methanol and dried in a vacuum oven at 60 °C for 3 days. The number-average molecular weight of the polymer was 85 000 by GPC, and the ratio M_w/M_n was calculated to be 2.5. In the second part of our study a low-molecular-weight-polystyrene (LPS) was synthesized by anionic polymerization at dry ice temperature, using butyllithium as initiator. The molecular weight of LPS was determined to be 2900 with an M_w/M_n ratio of 1.1. The glass transition temperature of the polymer was 66 °C.

(2) Film Preparation. Polymer films, about 24–27 μm in thickness, were prepared by casting from toluene solution onto glass slides. After solvent had been allowed to evaporate under ambient conditions for 1–2 h, the sample was dried in a vacuum oven for 3 days. Polystyrene was dried first at 60–70 °C and then at 110 °C, but PVME was dried only at room temperature to avoid the possibility of oxidation at higher temperatures. We also found in the course of our study that strict adherence to the above procedure of purification, drying, and storage was necessary for PVME in order to obtain reproducible results. Slight variations of the procedure suffice to bring about different oxidation results, although no chemical difference among samples can be detected by IR or NMR spectroscopy.

(3) Oxygen Uptake Measurement. The oxygen uptake measurement apparatus consists of a sample cell and a reference cell placed inside a heating block. The temperature of the block was controlled to within ±0.1 °C. Both cells were initially filled with oxygen to the same pressure of 770 mmHg. As oxidation proceeded, the amount of oxygen consumed by the sample was determined by monitoring the pressure difference between the two cells. During oxidation of PVME, gases were evolved at later stages of the experiments. The volatile products, mainly water vapor and carbon dioxide, were absorbed by calcium oxide that was placed in the cell but kept away from the sample by a wad of preoxidized Pyrex glass wool. Under the experimental conditions, film thickness had no effect on oxygen uptake as long as the thickness was less than 50 μm. Henceforth, films about 25 μm in thickness were used. Because, under the experimental conditions, the rate of oxygen diffusion was rapid, the oxidation reaction was not limited to the surface region. Oxygen uptake is expressed here as cubic centimeters (at 25 °C/1 atm) per gram of polymer.

(4) Separation of PS from PVME in the Oxidized Blend. A crucial part of our 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. Our procedure takes advantage of the solubility differences of the two polymers: poly(vinyl methyl ether) is soluble in methanol, which is a nonsolvent for PS. A solution of the oxidized blend in methylene chloride was added dropwise into methanol. After methylene chloride was allowed to evaporate, the mixture contained polystyrene as precipitate and PVME in the solution. The two phases were separated by using a centrifuge. The PVME solution was decanted, and the PS precipitate was rinsed with methanol at least five times. All methanol rinses were combined with the original supernatant and filtered through a 0.5-μm filter. Particles of PS remaining on the filter were combined with the PS precipitate. The effectiveness of this procedure was confirmed by GPC and FTIR measurements of unoxidized blends.

(5) Gel Permeation Chromatography. The molecular weights of the polymers were measured by using a Waters gel permeation chromatograph, Model 590. Tetrahydrofuran was used as the solvent, and nine PS standards were used for calibration. A differential refractometer was used for PVME measurement and a UV detector for PS.

(6) Differential Scanning Calorimetry. Glass transition temperatures of the component polymers and their blends were measured by a Du Pont Model 9900 thermal analyzer equipped with a differential scanning calorimeter. A heating rate of 10 °C/min was used for all thermal scans. The T_g values, taken as the midpoints of the specific heat jumps, were −27 for PVME, 106 for PS, −11 for the blend containing 65% by weight of PVME, 2 for the 50% blend, and 13 °C for the blend containing 35% PVME.

(7) Cloud Point Measurement. The procedure for determining cloud points was the same as that used previously.[10] A microscope equipped with a hot stage was used. The temperature at which the intensity of the transmitted light began to decrease was recorded as the cloud point. Sample thickness between 25 and 125 μm and a heating rate of 1 °C/min were found to be suitable. The cloud temperatures were 118, 123, and 131 °C for the 65, 50, and 35% blends, respectively.

(8) Infrared Spectroscopy. A Digilab FTS-60 FTIR spectrometer was used to monitor spectral changes during oxidation. A multimode cell, Accuspec Model 2000, which served as an oxidative chamber, was used. The sample was solution-cast onto a polished aluminum plate, dried, and placed on the end face of the heating probe. The chamber was first filled with nitrogen. After the sample was heated to the desired temperature, nitrogen was replaced by oxygen. Typical parameters for IR measurement were as follows: resolution of 4 cm^{-1}, scan number of 64, scan frequency of 20 kHz, and sensitivity of 1. The time required for 64 scans was 25 s.

A Shimadzu Model 435 infrared spectrometer was used for preliminary and general purpose experiments.

III. Results and Discussion

(1) Oxygen Uptake. Thermal oxidation experiments were carried out at 80, 110, and 140 °C. The two polymers were miscible at 80 and 110 °C but not at 140 °C. These temperatures were above the T_g's of the polymers (except for PS at 80 °C), so that segment mobility was not a limiting factor in the oxidation process.

Oxygen uptake data at 110 °C are shown in Figure 1. Polystyrene has been reported to have an induction period of longer than 10 000 h at 110 °C.[12] The amount of oxygen consumed by PS was too small to be measured during our experiments. However, PVME reacted with oxygen rapidly after an induction period of about 0.5 h. Once

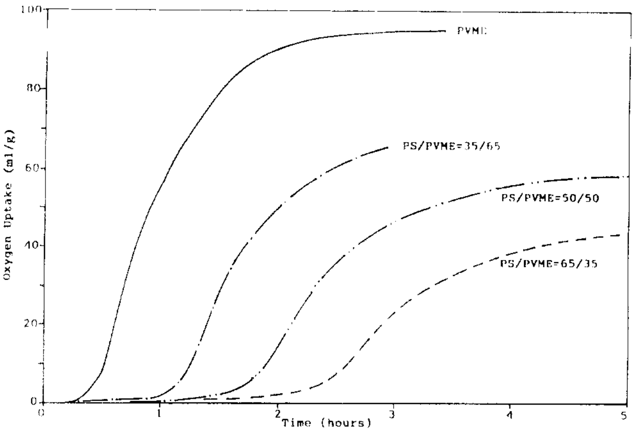

Figure 1. Oxygen uptake curves of PVME and its blends with PS at 110 °C.

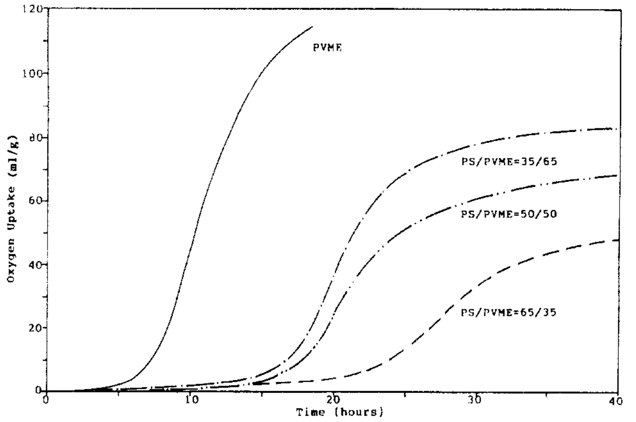

Figure 2. Oxygen uptake curves of PVME and its blends with PS at 80 °C.

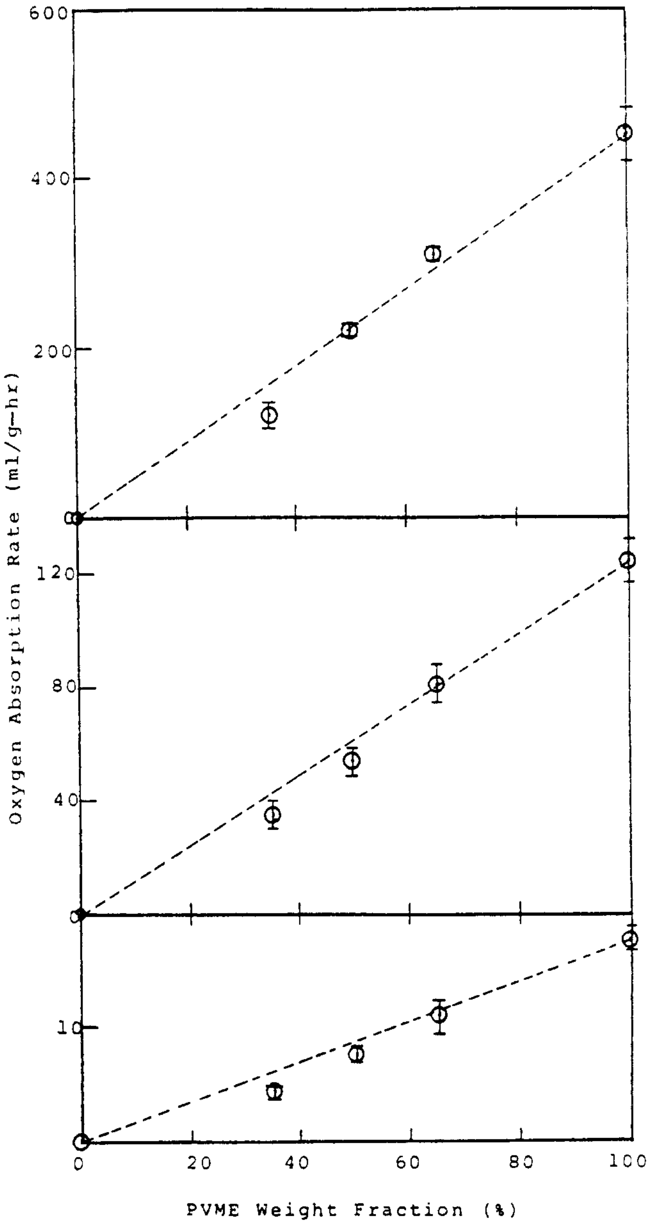

Figure 3. Steady-state oxygen absorption rates of PS/PVME blends: bottom, 80 °C; middle, 110 °C; top, 140 °C.

the induction period was exceeded, oxygen consumption proceeded at an approximately constant rate of 124 (mL/g)·h. After 60 mL/g was consumed, the oxidation rate began to decrease and gradually reached a saturation value of about 100 mL/g (as a reference point, absorption of 105 mL/g corresponds to one molecule of oxygen per four PVME repeating units). The shape of the curve was typical of autoxidation processes. For the three blends, curves of a similar shape were obtained, but the induction periods lengthened and the rates of oxidation decreased as PS contents increased. The saturation values were approximately proportional to PVME contents in the blends.

The consumption of oxygen by PS at 80 °C was negligible, as expected, but the oxidation of PVME still took place rapidly after an induction period of 8.3 h. The uptake was 80 mL/g at 13 h, after which the rate decreased, and a saturated region was reached at long times. For the three blends, again the induction periods lengthened and oxidation rates decreased as the PS content increased (Figure 2). Oxygen uptake experiments at 60 °C were not pursued because at this temperature the induction period for PVME was found to be longer than 14 days.

The lengthening of the induction period in the blend is suggestive of PS acting as an inhibitor. The steady-state rates of oxidation at both 80 and 110 °C, however, are approximately proportional to the PVME contents of the blends (Figure 3), as though PS has lost its inhibitory action in this region and the oxidation of PVME occurs independently of the presence of PS in the blend. Since PS was present in large quantities, the loss of inhibitory power after oxygen consumption of only 1–2 mL/g of PVME was at first puzzling. However, it was noticed that all the blend films turned opaque shortly before the ends of the induction periods. Apparently, phase separation had taken place during the early stages of oxidation. Once PVME and PS resided in separate phases, it became reasonable that the oxidation of PVME proceeded independently of PS and the steady-state rates became proportional to the PVME content in the blend.

While the above explanation gave a satisfactory account of the oxidation rates, the observation of phase separation after less than 2 mL/g of oxygen was consumed by the blend, or one molecule of oxygen per 100 PVME repeating units, required independent experimental verification. To this end, we preoxidized PVME for various time intervals at 110 °C and studied the miscibilities of the oxidized PVME with PS. The cloud point temperatures of blends of oxidized PVME and PS are shown in Figure 4. Poly(vinyl methyl ether), which had been oxidized for 20 min (about 2 mL/g), was no longer miscible with PS at 110 °C, and the polymer oxidized for 30 min (about 4 mL/g) was immiscible with PS at 80 °C. These results demonstrated that small changes in the chemical structure of PVME caused by one to two molecules of

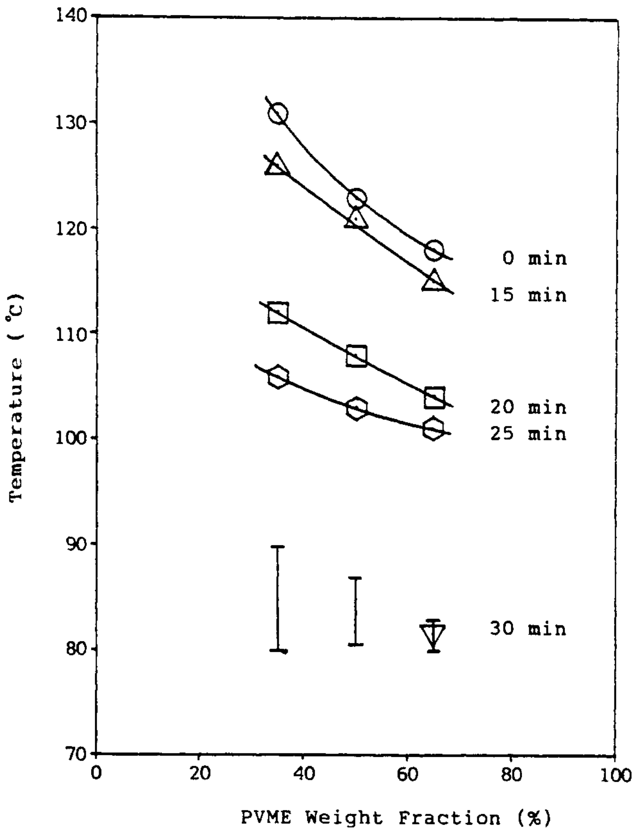

Figure 4. Cloud point curves of blends of PS with preoxidized PVME.

oxygen per 100 repeating units altered profoundly the miscibility behavior. That minor changes in the structure of the polymer suffice to alter miscibility behavior drastically is not totally surprising because it has been shown that PS becomes more miscible with PVME upon replacement of the aromatic hydrogen atoms by deuterium.[11]

Additional support for our interpretation was found in the results of oxidation experiments carried out at 140 °C, at which temperature the blends underwent phase separation even in the absence of oxygen. One would then expect the induction periods to be less sensitive to PS content because PS now resided predominantly in a different phase. (This statement is not strictly correct because phase separation does not result in pure phases, but it is a useful approximation in the present context.) Indeed, at 140 °C we found the induction periods for PVME and the three blends to have about the same value of 0.05 h and the oxidation rates to be proportional to PVME content (Figure 3). Furthermore, Arrehenius plots of oxidation rates at the three different temperatures yielded essentially parallel straight lines for PVME and the blends (Figure 5). The identical activation energies in the steady-state regions speak strongly of a common reaction mechanism for PVME and the blends and are consistent with the phase-separation phenomena.

(2) Molecular Weight Changes. The next phase of our study concerns the changes in the molecular weight of the polymers during oxidation. The results of MW measurements are shown in Figure 6 for PVME after oxidation at 110 °C. The molecular weight of PVME decreased very rapidly during the first hour of oxidation to below 2000, which was beyond the range of efficiency of the chromatographic columns used. The molecular weight changes of PVME in the blends occurred more slowly and bore comparison with the oxygen uptake curves.

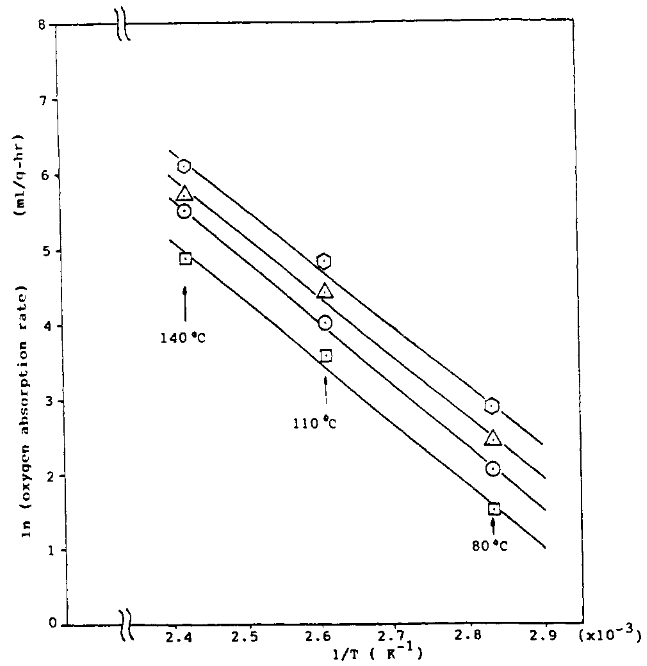

Figure 5. Arrhenius plots of steady-state oxygen absorption rates for PVME (top) and its blends with PS.

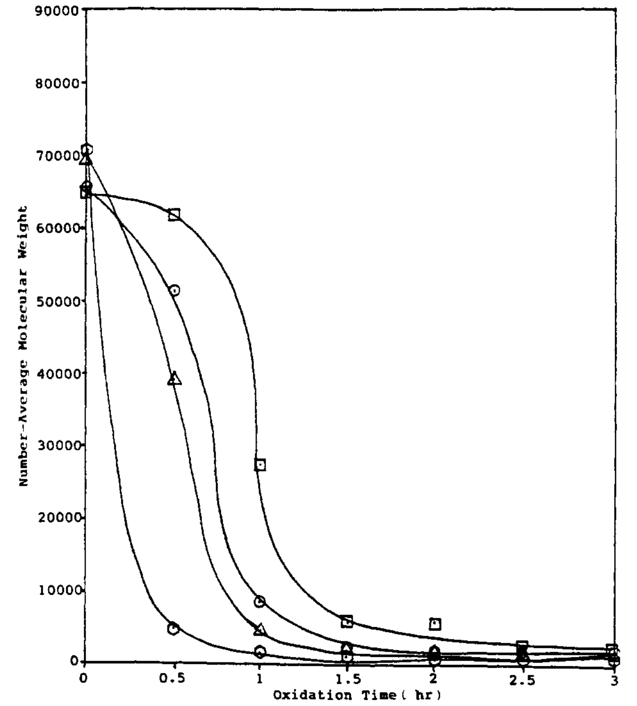

Figure 6. Changes in the molecular weight of PVME as a function of oxidation time at 110 °C (values below 2000 are inaccurate). PVME contents are as follows: ○, 100%; △, 65%; ○, 50%; □, 35%.

It is worthy of note that a 15-fold decrease in the molecular weight of PVME has occurred during the induction period in all four cases. Since miscibility is favored by low molecular weight, the cause of phase separation observed here can only be attributed to chemical changes.

Polystyrene itself showed only minor molecular weight changes after oxidation. The number-average molecular weight increased from the original value of 85 000 to 97 000 after oxidation at 110 °C for 48 h and to 112 000 after oxidation at 140 °C for the same period of time. However, a twofold decrease was found in the oxidized blends (Figure 7). The twofold decrease corresponded to an average of one main chain scission per molecule,

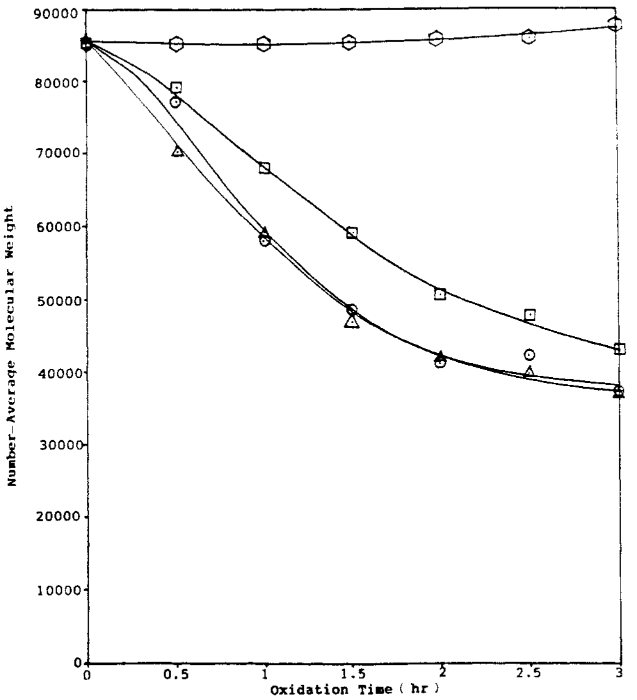

Figure 7. Changes in the molecular weight of PS as a function of oxidation time at 110 °C. PS contents are 100, 65, 50, and 30% from the top to the bottom curves.

i.e., one scission per 820 repeating units. The chemical changes caused by one scission per 820 units were not detectable by FTIR or NMR spectroscopy. Molecular weight determination appeared to be the only effective but simple method to detect changes in PS.

The changes in the molecular weight of PS provide the important clue that PS is directly involved in the oxidation of the blends. When this observation is viewed in conjunction with the lengthening of the induction period, the conclusion is reached that a reaction between PVME radicals probably of the peroxy type and PS must have taken place. The resulting PS radical is less reactive[12-14] and causes the retardation of the oxidation process in much the same way as an antioxidant radical, although the detailed mechanism of retardation remains to be elucidated. The first-formed PS radical or a radical derived therefrom eventually undergoes scission to result in a decrease in the molecular weight.

Although the decreases in PS molecular weight occurred primarily during the induction periods, the changes seemed to continue, to some extent, even after phase separation. This is thought to be due to contacts between the two polymers in the boundary regions of different domains and/or to the presence of two phases containing finite concentrations of each component. The former effect was proposed by Scott[3] for rubber-modified polystyrene.

(3) Changes in Chemical Structure. The FTIR spectra of oxidized PVME (Figure 8) showed OH(OOH), C=O, and C=C peaks that increased in intensity during oxidation. The broad peak at 3200–3500 cm^{-1} is believed to be the absorption of hydroxyl and hydroperoxide groups. Our attempt to assess the hydroperoxide content by reaction with sulfur dioxide to form hydrogen sulfate[15,16] was not successful because there was only a minor decrease in the original absorption and the new peak overlapped with the strong C–O absorption near 1100 cm^{-1}. The band at 1739 cm^{-1} represents the absorption of several different carbonyl groups, but the peak location suggests ester carbonyl as the dominant species.[17-20] Since the α-hydrogen of PVME should be easily abstracted, subsequent reactions involving hydroperoxide formation and decomposition followed by β-scission of the alkoxy radical provide a plausible path to ester formation. Besides the absorptions described above, other broad bands are present in the 1000–1400 cm^{-1} region. These absorptions are believed to be due to C–O stretching and O–H deformation vibrations of alcohols and their associated forms.[17] The PVME polymer separated from the oxidized blends had qualitatively similar spectra. Both PVME and the blends became yellowish after oxidation. The formation of conjugated double bonds was suggested by the color, but no attempt was made to determine the conjugation length.

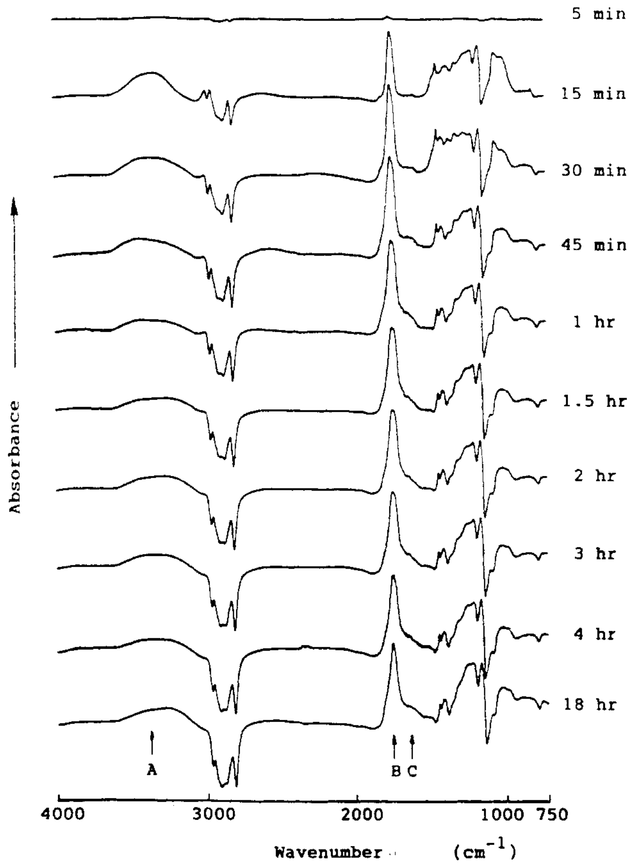

Figure 8. FTIR spectra of oxidized PVME.

In order to determine the changes in the OH(OOH) and C=O absorptions with time, difference spectra of the oxidized PVME were obtained by subtracting the spectra of the original PVME from that of the oxidized polymer (Figure 8). (The subtraction factor was 1.00 after base-line correction.) The distinctive features of Figure 8 are the growing intensities of the OH(OOH), C=O, and C=C peaks at the expense of the CH, CH_2, and CH_3 peaks in the 2800–3000 cm^{-1} region.

Changes in the peak areas of the OH(OOH) and C=O bands with time are plotted in Figure 9. The trend of the changes in hydroxyl/hydroperoxide concentration with time is in general agreement with the results of the oxidation of other polymers.[21-23] The accepted interpretation is that hydroperoxide groups accumulate during the induction period and eventually reach a maximum concentration. Autoacceleration starts as hydroperoxide groups decompose into initiating radicals. Nevertheless, there are deviations from the general description.[19] In our case, the maximum concentration of hydroperoxide was reached at 0.5 h, which was the end of the induction period. We are not certain whether this observa-

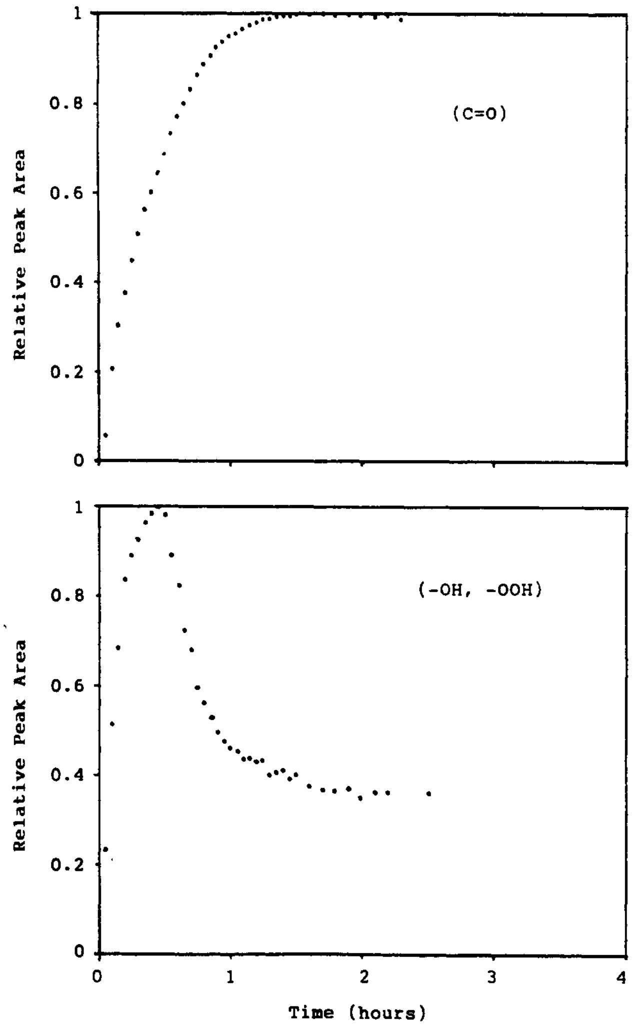

Figure 9. Concentrations of (-OH/-OOH) and (C═O) groups during PVME oxidation at 110 °C.

tion is merely a result of the inherent difficulty in the exact determination of the peak area.

The carbonyl peak increased in intensity continuously and then leveled off after 1 h. Since carbonyl groups are formed through β-scission of alkoxy radicals, there is a close relationship between the carbonyl group concentration and the decrease in MW shown in Figure 6. This relation was reported by Iring et al. for polyethylene.[24]

The temporal evolution of OH(OOH) and C═O groups in the blends was almost the same as for PVME itself, even though there were obvious differences in induction periods. We believe that this result is partially due to the preferential presence of PVME at the surface.[25,26] Since reflectance spectra were recorded in our study, the contribution of PVME at the surface was disproportionately emphasized.

(4) Blends Containing Low-Molecular-Weight Polystyrene (LPS). Since phase separation intervened in the oxidation of the blends, it was thought important to devise a system which remained homogeneous throughout the reaction. The use of low-molecular-weight polystyrene (M_n = 2900) served the purpose. The oxygen uptake of LPS blends at 110 and 140 °C is shown in Figures 10 and 11, respectively. The induction periods were longer and the oxidation rates lower than the values for the corresponding PS blends. Furthermore, the rates were not proportional to PVME contents (Figure 12). The significantly lower oxidation rates, taken together with the longer induction periods, are compelling evidence of LPS participation in both stages of the oxidation reaction. The superior effectiveness of LPS in retarding the oxidation of PVME is simply a consequence of the retention of miscibility between LPS and oxidized PVME.

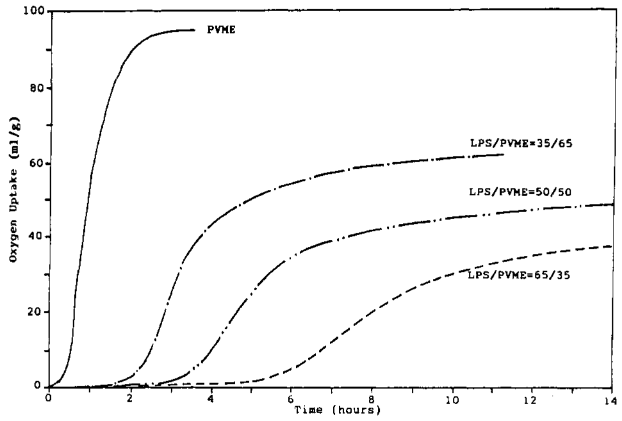

Figure 10. Oxygen uptake curves of blends of PVME with low-molecular-weight polystyrene (LPS) at 110 °C.

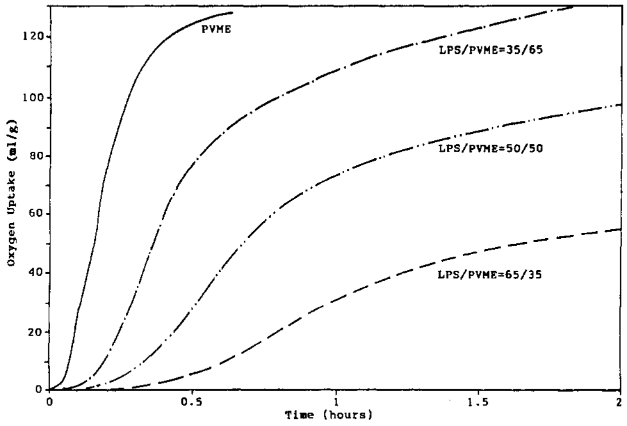

Figure 11. Oxygen uptake curves of blends of PVME with LPS at 140 °C.

The slower oxidation rates in LPS blends may come about as a result of reduced propagation rates or increased termination rates or both. We note that the apparent activation energies in the steady-state region are the same for the three LPS blends, namely, 21 kcal/mol. This quantity is much larger than the value of 16 kcal/mol for PVME itself and for PS blends. On the other hand, the temperature coefficients of log t_{ind} of PVME and LPS blends, where t_{ind} is the induction period, differ by only about 15%. Further study is needed to understand these differences.

Since LPS blends remained as single phases during oxidation, the enhanced possibility of cross-propagation and cross-termination reactions would result in more extensive changes in the chemical structure of LPS. An attempt was therefore made to separate LPS from an oxidized 50/50 blend by using the same method of PS precipitation described earlier. However, the LPS in the oxidized blend did not precipitate easily, and some of the precipitated material was dissolved in methanol after repeated rinsing. This observation itself could be considered as evidence of substantial chemical changes in LPS. A LPS sample with a MW of 500 is soluble in methanol, but a sample with a MW of 1000 is not.

A second experiment consisted of extraction of the oxidized blend by methanol in a Soxhlet apparatus. Extraction was carried out for 5 days under argon atmosphere. (Even under argon atmosphere, additional oxidation of PVME occurred to a slight extent, but this did not affect

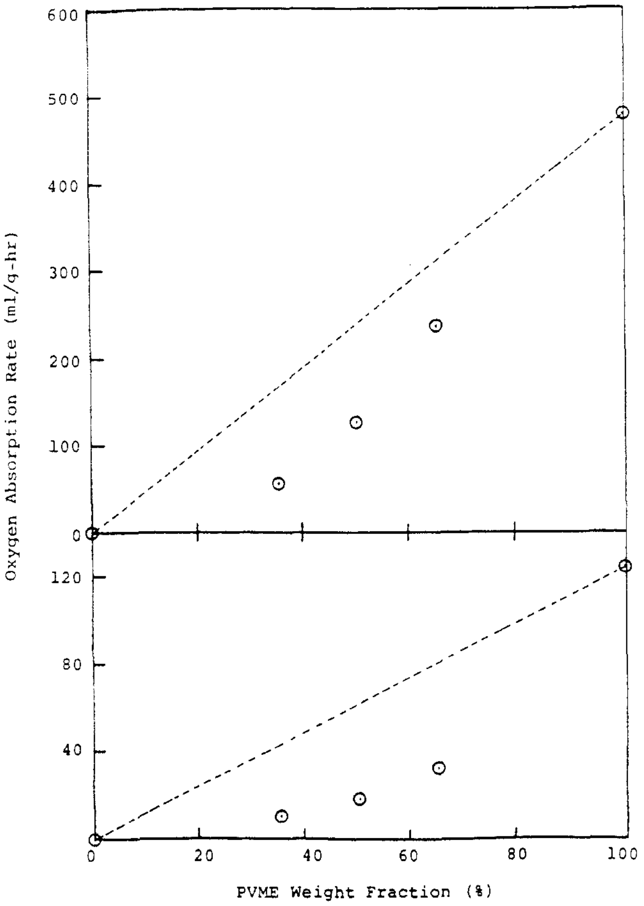

Figure 12. Steady-state oxygen absorption rates of PVME/LPS blends: bottom, 110 °C; top, 140 °C.

our results.) The FTIR spectra of the extracts from the virgin and oxidized 50/50 blends are shown in Figure 13. The extracted material is composed mainly of oxidized PVME. Small peaks above 3000 cm^{-1} are due to aromatic C–H stretching, indicating the presence of LPS. It is seen that a small amount of LPS also appears in the extract from the unoxidized blend due to the slight solubility of LPS in refluxing methanol. The LPS absorbance, however, is definitely much stronger for the extract from the oxidized blend. The increased solubility of LPS is most likely due to the introduction of oxygen-containing groups into LPS, but the possibility of attachment of PVME onto LPS through cross-termination reactions cannot be ruled out. With regard to the former possibility, Ohkatsu[27] found that poly(*p*-isopropylstyrene) showed some solubility in methanol after oxidation.

In the FTIR spectra of oxidized LPS blends, the area of OH(OOH) absorption could not be determined accurately due to difficulties encountered in drawing base lines. The carbonyl absorption region, however, was not encumbered with this problem. The changes in the carbonyl peak area in the LPS blends are shown in Figure 14. The time needed to reach the maximum peak area increases as LPS content increases, and 50–90% of the carbonyl groups are formed during the induction periods. These results differ from the findings for PS blends.

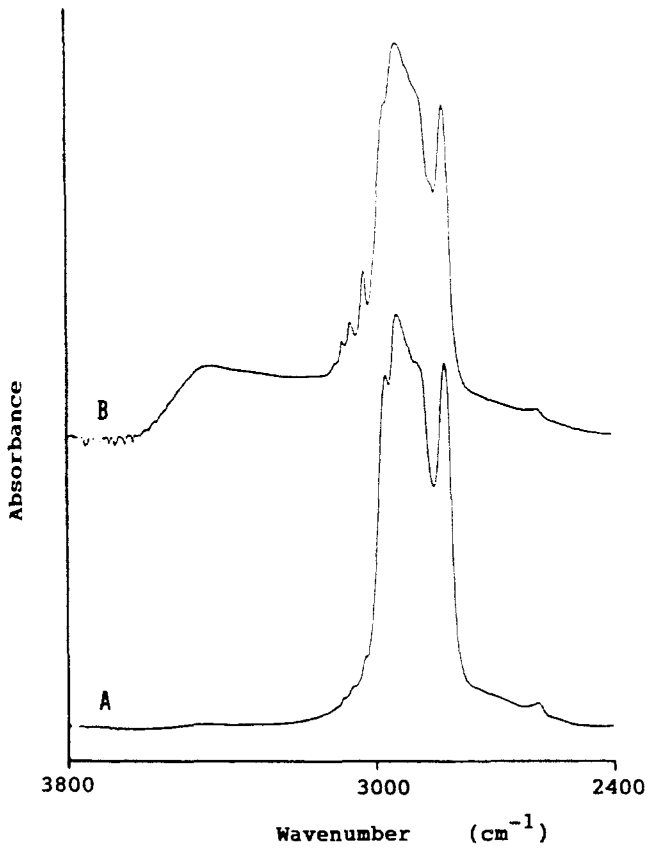

Figure 13. FTIR spectra of methanol extracts of PVME/LPS blends: A, before oxidation; B, after oxidation at 110 °C.

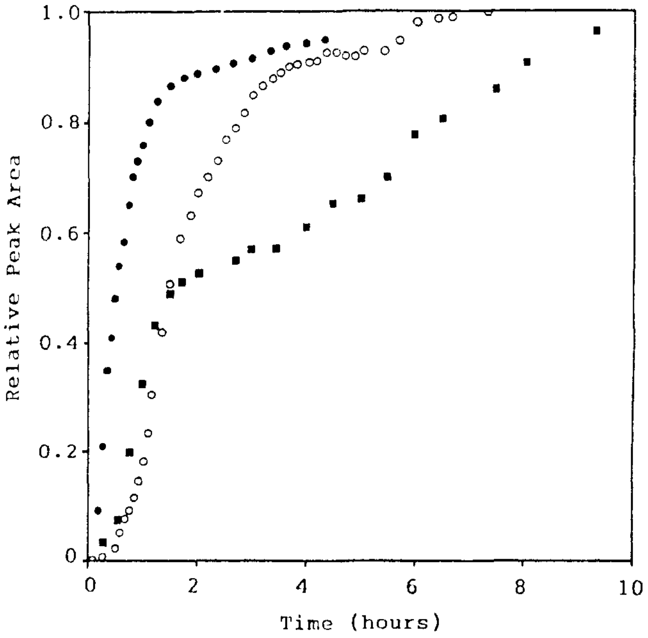

Figure 14. Carbonyl group absorption as a function of time during oxidation of PVME/LPS blends at 110 °C: ●, 65% PVME; ○, 50%; ■, 35%.

IV. Conclusions

Several major conclusions can be drawn from the experimental results for PS/PVME blends: (1) The induction period of thermal oxidation of PVME was lengthened by the presence of PS. (2) Phase separation occurred shortly before the end of the induction period. At the point of phase separation, PVME was oxidized only to the extent of about one oxygen molecule per 100 repeating units. (3) As a result of phase separation, the steady-state rate of oxidation was proportional to the PVME content in the blend. (4) The molecular weight of PVME decreased more slowly in the blends as PS content increased. Polystyrene, which suffered no decrease in MW by itself, experienced chain scission in the blend. (5) Reaction between PVME radicals and PS took place during the induction period, most likely through the abstraction of the tertiary hydrogen atom of PS. The resulting PS radical, being less reactive in chain propagation, caused the retardation of the oxidation reaction.

When low-molecular-weight polystyrene was blended with PVME, the mixtures remained homogeneous throughout the oxidation reaction. The induction periods were longer and the oxidation rates slower than the values for the corresponding PS blends. Low-molecular-weight polystyrene was involved in the oxidation process both during the induction period and in the steady-state region. Cross-propagation and/or cross-termination reactions between PVME and LPS resulted in changes in the solubility, and presumably the chemical nature, of LPS.

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A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 1. Application to Di-*n*-alkyl Phthalates in PVC

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ABSTRACT: The standard free volume theory of the diffusion of small molecules in amorphous polymers above T_g has been extended to include the fundamental motions of comparatively large molecules such as plasticizers. In addition to accounting for liberated penetrant translational entropy, a new feature consisting of an elementary displacement of the molecule that is but a fraction of its long dimension is introduced. An effective diffusion coefficient is derived for elongated molecules which is the result of averaging over probable penetrant jumps from zero up to the entire molecular length. While a necessary plasticizer efficiency parameter presently must be determined by experiment, the theory requires a minimal input database of readily accessible quantities and involves no adjustable parameters. An application of the rough theory to the di-*n*-octyl and di-*n*-decyl phthalate in PVC systems shows encouraging results.

Introduction

A general theory of the diffusion of extraordinarily large molecules in rubbery amorphous polymers is of interest, not only from the standpoint of scientific understanding but also with regard to material design and process optimization. Clearly, a broadly applicable model would be of extreme utility in consideration of the controlled trans-