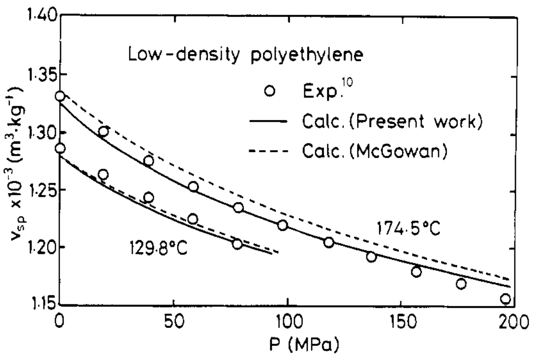

Figure 3. Specific volumes of low-density polyethylene.

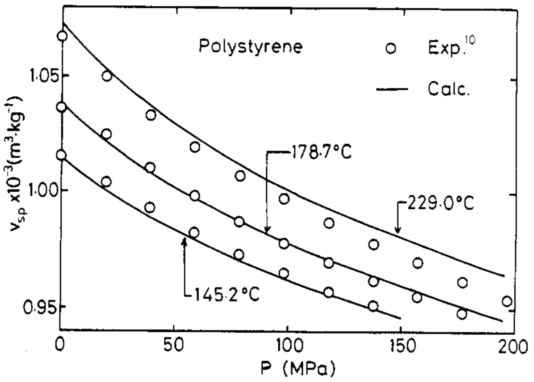

Figure 4. Specific volumes of polystyrene.

$v^*_{sp} = \{13.7 \times 10^{-6} \times 0.042 + 10.2 \times 10^{-6} \times (1 - 0.042)\}/\{15 \times 10^{-3} \times 0.042 + 14 \times 10^{-3} \times (1 - 0.042)\} = 0.7369 \times 10^{-3}$ m^3·kg^{-1}, $T^* = (4640 \times 0.5529/0.03964)^{1/1.23} = 8155$ K, and $P^* = 0.03964 \times 8.314 \times 8155/\{13.7 \times 10^{-6} \times 0.042 + 10.2 \times 10^{-6} \times (1 - 0.042)\} = 259.7$MPa, where Q is the UNIFAC area parameter.[7] For comparison, the results calculated with McGowan's equation[12] ($21P'/M' = 59.8$, $T'_c = 403$ K) are also shown in Figure 3. The value of T'_c is determined to give a good fit for the experimental specific volumes. It seems the present results are slightly better.

For the case of polystyrene, it is difficult to estimate the one-third external degrees of freedom per repeating unit. As shown in Table I, the value of C_k for the end group of the hydrocarbon chain (CH_3) is much larger than that for the middle group in the hydrocarbon chain ($CH(CH_3)$ or $C(CH_3)_2$). Therefore, it is reasonable to consider that the external degrees of freedom for the phenyl group attached to the main chain is smaller than that for benzene. The one-third external degrees of freedom per repeating unit was determined as 0.25 by fitting the calculated results to specific volumes of polystyrene. The values of the parameters for polystyrene are calculated as $v^*_{sp} = (10.2 \times 10^{-6} + 8.1 \times 10^{-6} \times 5 + 12.3 \times 10^{-6})/104.152 \times 10^{-3} = 0.6049 \times 10^{-3}$ m^3·kg^{-1}, $T^* = \{(4640 \times 0.768 + 7510 \times 2.120)/0.25\}^{1/1.23} = 9485$ K, $P^* = 0.25 \times 8.314 \times 9485/(10.2 \times 10^{-6} + 8.1 \times 10^{-6} \times 5 + 12.3 \times 10^{-6}) = 312.9$ MPa. The results calculated with these parameters are in good agreement with the experimental data[10] as shown in Figure 4. It is noted that application of the present equation of state is limited to liquid states.

Summary

A semiempirical equation of state has been developed to predict specific volumes of molten polymers and low molecular weight hydrocarbon liquids. The values of the parameters needed in the prediction can be obtained by summing up group parameters alone. The group parameters are reported for aliphatic and aromatic hydrocarbons. The specific volumes of molten polymers such as low-density polyethylene and polystyrene can also be calculated by use of the group parameters. However, the one-third external degrees of freedom per repeating unit for polystyrene should be adjusted to obtain good results.

Registry No. Polyethylene (homopolymer), 9002-88-4; polystyrene (homopolymer), 9003-53-6; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; benzene, 71-43-2; toluene, 108-88-3; *m*-xylene, 108-38-3.

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Activation of Epoxide Polymerization under Ultraviolet Radiation

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Conversion of epoxide to polymer was found to increase significantly under UV irradiation in the presence of a tris(β-diketonato)aluminum (Al-I) and triphenylsilanol, which we have already described.[1] Also we have reported[2–4] the initiation mechanism of the polymerization of epoxides by these catalysts.

Results obtained with cyclohexene oxide and three aluminum-based catalysts[6] are shown in Figure 1. In the case of tris(2,4-pentanedionato)aluminum (Al(acac)$_3$) and triphenylsilanol catalyst, conversion to polymer under UV irradiation was about 3–5 times higher than that in the dark. The temperature change of the polymerization system caused by UV radiation with a mercury lamp was negligible.

An increase in polymer conversion under UV irradiation was also observed when the Al-I complexes tris(1,1,1-trifluoro-2,4-pentanedionato)aluminum (Al(tfp)$_3$) and tris(2,6-dimethyl-3,5-heptanedionato)aluminum (Al(dmh)$_3$) were employed (Figure 1). The increase was remarkable when an aluminum complex substituted with an electron-donating group on the carbon bonded to the carbonyl carbon, such as Al(dmh)$_3$, was used.

The molecular weight of the polymer polymerized with (Al(acac)$_3$)/triphenylsilanol catalyst for 60 min under the same conditions shown in Figure 1 was measured by gel permeation chromatography with a Toyo Soda Type 801 apparatus (column constitution, G-2000H$_8$, G-2000H$_8$, G-3000H$_8$, and G-4000H$_8$ (polystyrene gel)) by elution with THF at 40 °C. Calibration was carried out with standard polystyrene mixtures. M_n and M_w, which were 13 000 and 35 000, respectively, in the dark, increased to 21 000 and

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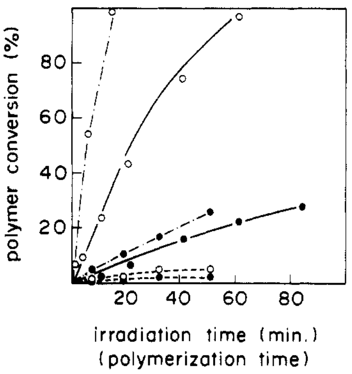

Figure 1. Polymerization of cyclohexene oxide with (Al-I)/triphenylsilanol catalyst under UV irradiation with a 400-W high-pressure mercury lamp and ($Al(acac)_3/Ph_3SiOH$) or a 60-W low-pressure mercury lamp and ($Al(tfp)_3$,$Al(dmh)_3/Ph_3SiOH$), in N_2: (—) $Al(acac)_3/Ph_3SiOH$ (0.03 mol %/0.03 mol %) at 40 °C; (– – –) $Al(tfp)_3/Ph_3SiOH$ (0.03 mol %/0.05 mol %) at 35 °C; (–·–) $Al(dmh)_3/Ph_3SiOH$ (0.03 mol %/0.03 mol %) at 35 °C. (●) in the dark; (○) under UV irradiation.

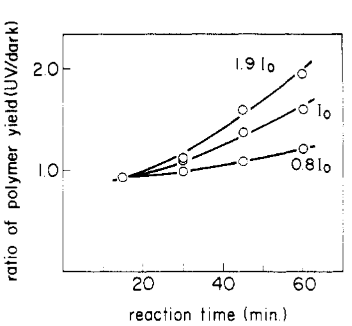

Figure 2. UV strength dependence on polymer yield. Monomer, cyclohexene oxide; catalyst, $Al(acac)_3$, 0.03 mol %, triphenylsilanol, 0.03 mol%; polymerization temperature, 40 °C; UV intensity, I_0, in an N_2 low-pressure mercury lamp. The UV intensity was varied by use of UVL 10 LA, UVL 30 LA, or UVL 60 LA.

42000, and M_w/M_n decreased from 2.7 to 2.0 when 254-nm light was used. Termination was presumed to occur by addition of silanolate anion to the epoxy ring and H^+ subtraction from the propagating polymer site by silanolate anion, which then forms silanol.[3] Basicity of the silanolate anion may be reduced under the excited state, and it may be more difficult for termination to occur under UV radiation compared with in the dark.

The atmosphere in the polymerization tube affected the polymer yield under UV irradiation. The yield of the polymer polymerized by the use of $Al(acac)_3$/triphenylsilanol catalyst at the concentration of 0.035 mol % to cyclohexene oxide for 60 min at 40 °C was 99% in dry N_2 but 32% in dry air. O_2 might quench the excited state of the catalyst produced by UV irradiation.[6]

In the case of tris(β-carbonyl esterato)aluminum (Al-II) such as tris(ethyl 3-oxobutanoato)aluminum ($Al(etaa)_3$), and tris(salicylaldehydato)aluminum ($Al(sa)_3$) (Al-III), the polymer conversion under UV irradiation was somewhat less than that in the dark. Therefore, the increase in the conversion to polymer when $Al(acac)_3$/triphenylsilanol was used is explained in terms of the catalyst activation and not in terms of the activation of cyclohexene oxide monomer by UV irradiation.

UV irradiation at a wavelength of 254 nm was found to be effective for the activation of the catalyst. When 0.03 mol % of cyclohexene oxide was polymerized with 0.03 mol % of $Al(acac)_3$/triphenylsilanol for 70 min at 40 °C, the ratio of the polymer conversion under 254-nm irradiation to that in the dark was 2.7. However, polymer conversion under irradiation at wavelengths greater than 365 nm was the same as that in the dark.

Figure 2 shows the UV intensity dependence on the polymer conversion, in which the terms $1.9I_0$, I_0, and $0.8I_0$ are relative UV intensities. The ratio of polymer conversion under UV irradiation to that in the dark increased with an increase in the intensity of UV light.

The most interesting point is that the increase in the polymer yield under UV irradiation was observed only when (Al-I)/silanol catalyst was used. (Al-II)/silanol or (Al-III)/silanol catalyst did not increase the polymer conversion, even if UV light was used. There are two possible explanations for the difference in the phenomena.

One relates to the difference in the initiation mechanism, which was already reported.[3] In the case of (Al-I)/triphenylsilanol, the H of the SiOH is detached from the oxygen when the H of the SiOH interacts with carbonyl oxygen, which chelates the aluminum atom. The H is polarized to form H^+, which polymerizes the epoxide cationically. There is no reaction, such as ligand exchange, between the aluminum complex and the triphenylsilanol. In the case of (Al-II)/triphenylsilanol or (Al-III)/triphenylsilanol, a part of the aluminum complex reacts with a part of the triphenylsilanol to form a compound that contains a Si–O–Al linkage. This is a kind of ligand-exchanging reaction and equilibrium reaction. Then the H of SiOH, which was not consumed by the reaction of the aluminum complex, is detached from the oxygen when the oxygen atom of SiOH interacts with the aluminum atom of the Si–O–Al linkage. The H is polarized to form H^+, which polymerizes epoxide cationically. The interaction is similar to that of a silica–alumina catalyst. Therefore, the difference in the initiation mechanism is concerned with whether the interaction occurs between H and O or between Al and O. Our results show that the increase in the polymer conversion when UV light was used occurs only in the case of an interaction between H and O. Perhaps, when an excited state complex is being formed, detachment of H proceeds greatly under UV radiation only in the case of interaction between H and O, which increases the polymer yield greatly. We have little information on the excited state. Presumably, aluminum complex or triphenylsilanol is not excited, but the complex containing the aluminum complex and the silanol is excited under UV radiation. The largest activity change of $Al(dmp)_3$/triphenylsilanol could be explained by the assumption that the interaction between $Al(dmh)_3$ and silanol changes the most drastically under UV irradiation because $Al(dmp)_3$, which is substituted by the electron-donating group on the carbon bonded to the carbonyl carbon, makes the H of silanol detach from the O–Si group more easily than $Al(acac)_3$ or $Al(tfp)_3$.

The results that the polymer conversion increased with an increase in intensity of UV light also support this explanation.

The other reason for the increase in the conversion to polymer under UV irradiation is that the reaction between (Al-I) and triphenylsilanol proceeds only slightly under UV irradiation to form a small amount of Si–O–Al linkages. We have already described that the activity of the catalyst that consists of an aluminum complex with an Al–O–Si linkage and silanol is higher than that of the catalyst that consists of (Al-I) and silanol[4] because the interaction between the Al–O–Si linkage and silanol is stronger than that between (Al-I) and silanol. The catalyst activity is affected by both the amount of the Si–O–Al linkage and the amount of the remaining triphenylsilanol that was not consumed by the reaction of the aluminum complex. Therefore, an excess reaction of the aluminum complex with silanol causes a lack of silanol in the polymerization system and decreases the catalyst activity.[3] In the case of (Al-I), the formation of the Si–O–Al linkage is presumed to be very small compared with the case of (Al-II) and (Al-III). Therefore, the decrease of silanol by reaction between the aluminum complex and silanol must be negligible. On the other hand, in the case of (Al-II) and (Al-III), a part of the silanol reacts with a part of the aluminum complex even in the dark, and the amount of the silanol that does not react with the aluminum complex is determined by the equilibrium constant. However, when UV light is used, presumably, there is a lack of silanol in the polymerization system because the reaction of silanol with (Al-II) or (Al-III) is promoted under UV radiation. We tried to find an increase in the ligand-exchange reaction after UV irradiation by use of ^{1}H NMR spectroscopy. However, there was no difference in the ratio before and after UV radiation. The ratio of the ligand exchange under UV irradiation might change immediately to that measured in the dark, even if the ligand-exchange reaction is promoted under UV irradiation. There is no evidence on ligand exchange under UV radiation; however, it might be possible under UV radiation if the aluminum complex is labile under UV radiation.[7]

In conclusion, this paper reports the fact that polymerization proceeds faster under UV radiation only when a catalyst with a definite structure is used. The difference in polymerization behavior supports the difference in initiation mechanism, which was already reported.

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(5) UV irradiation was carried out by the use of a merry-go-round type UV irradiation apparatus (Riko-RH400-10W, Riko Kagaku) with a 400-W high-pressure mercury lamp (UVL 400H, Riko Kagaku) or a low-pressure mercury lamp (UVL 10LA, UVL 30LA, or UVL 60LA). The lamp was surrounded by a water-cooled quartz photolysis well. Samples were placed in the "merry-go-round" holder, which rotates around the lamp to provide even irradiation during photopolymerization. The entire apparatus was immersed in thermostated water at 40 °C. Light of 365 nm was radiated through a UVL-36 filter (Riko Kagaku) by means of a 400-W high-pressure mercury lamp.

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Comparison of the Pure Reptational Times Calculated from Linear Viscoelasticity and Diffusion Motion Data of Nearly Monodisperse Polymers

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A recently proposed general linear viscoelastic theory[1] indicates that the primitive chain contour length fluctuation (the $\mu_B(t)$ process) is responsible for the most part for stress decline in the plateau region of a step strain–stress relaxation. In the terminal region, the observed reptational motion is modified because of the same chain length fluctuation effect. From an analysis of the linear viscoelastic relaxation data of nearly monodisperse polymers in terms of the general theory, it was shown that these effects due to chain contour length fluctuation are the major factors causing the difference between the observed molecular weight (MW) dependence of zero-shear viscosity ($\eta_0 \propto M^{3.4}$) and that predicted by the reptational chain model ($\eta_0 \propto M^3$). In the low-MW region ($M_w < 7M_e$) two additional fast dynamic processes, the Rouse chain motion between two cross-linked points and the chain slippage through entanglement links, need be included. Furthermore, it was concluded that the constraint release effect on the linear viscoelastic relaxation is negligible as far as a very narrow molecular weight distribution (MWD) is concerned.

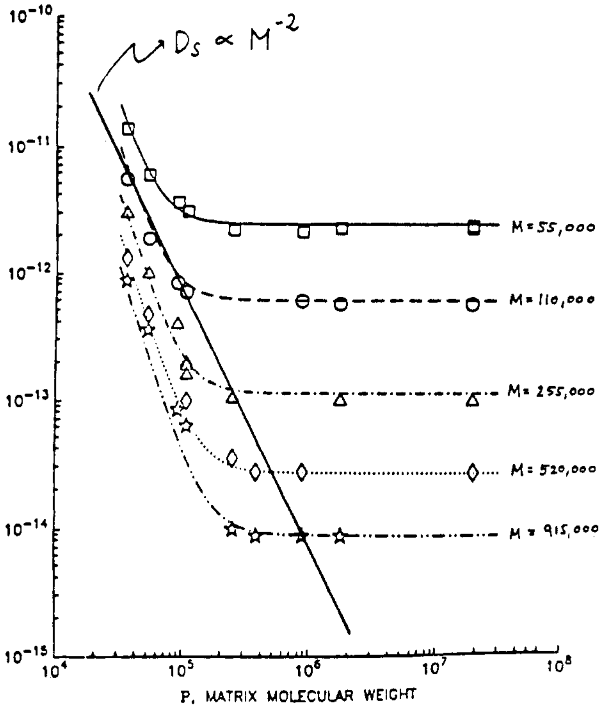

Figure 1. Tracer diffusion constant D of deuterated polystyrene of molecular weight M diffusing in polystyrene of molecular weight P vs. P (Reprinted with permission from ref 2. Copyright 1984 The American Physical Society). The straight line indicating the molecular weight dependence of the self-diffusion constant, D_S, has a slope of −2 (see text).

In this report, the pure reptational times at different MW's are calculated from the polymer diffusion constants obtained recently by Kramer's group at Cornell University using forward recoil spectrometry[2] and compared with those calculated from the linear viscoelastic results analyzed and reported previously.[1] Very good agreement has been obtained between these two different types of measurements, which were done independently. In the comparison, the physical significance of the relaxation times, especially as related to the possible role played by the constraint release in different conditions, is described.

Kramer et al. have measured the diffusion motion of a thin layer of a deuterated polystyrene (the labeled molecules) into a hydrogenated polystyrene base (the matrix). In their thorough study, they have varied both the MW of the labeled polymer and the matrix polymer. For a labeled polymer, if the MW of the matrix polymer is higher than a certain value (P_c), the measured diffusion constant is independent of the matrix MW. In other words, in such

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