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(14) When polynorbornene (70:30 trans/cis) was epoxidized using ca. 25% as much Oxone as that described in ref 13, the reaction was 50% completed (once again we noted the cis olefin was more reactive than the trans olefin).

Mark Lautens,*[1] Alaa S. Abd-El-Aziz, and Gunther Schmidt

Department of Chemistry, University of Toronto
Toronto, Ontario, Canada M5S 1A1

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Complex Formation between Poly(ethylene glycol) and α-Cyclodextrin

Since the discovery of cyclodextrins (α-CD, β-CD, and γ-CD), a great number of inclusion complexes with low molecular weight compounds, both organic[1] and inorganic,[2] have been prepared and characterized. However, there are no reports, to our knowledge, on the formation of complexes of CDs with polymers except for the examples in which a monomer was polymerized in situ within a cyclodextrin complex.[3,4] We have found that α-cyclodextrin forms complexes with poly(ethylene glycol) (PEG) of various molecular weights to give stoichiometric complexes in high yields.

When aqueous solutions of PEG were added to a saturated aqueous solution of α-CD at room temperature, the solution became turbid and the complexes were obtained as precipitates when the average molecular weight of PEG was between 400 and 10 000. This is the first observation that cyclodextrin forms complexes with polymers in a solid state. α-CD does not form complexes with the low molecular weight analogues, ethylene glycol,[5] diethylene glycol, and triethylene glycol. β-CD did not form complexes with PEG of any molecular weight.

The rate of the complex precipitation depends on the molecular weight of PEG. The rates were followed by absorbance at 700 nm. Figure 1 shows the effects of molecular weights on the rates of the turbidity development after mixing the α-CD solution and PEG solution. The

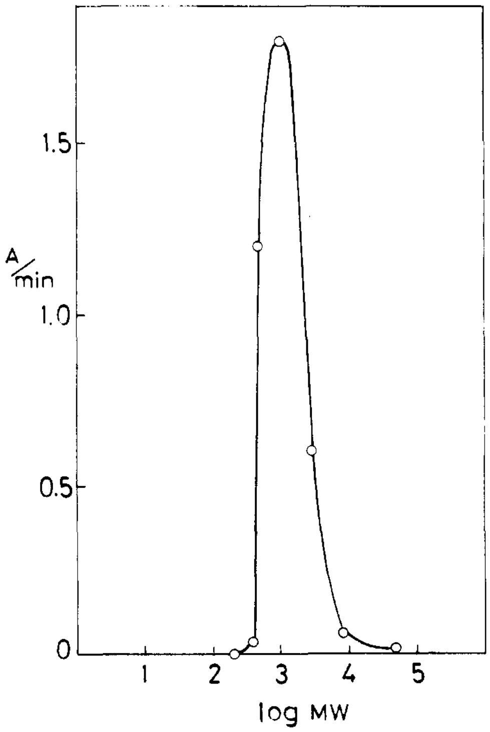

Figure 1. Rate of turbidity development after mixing the saturated α-CD solution and PEG solution. α-CD solution 2 mL, 10 mg of PEG/0.1 mL of H_2O, monitored at 700 nm.

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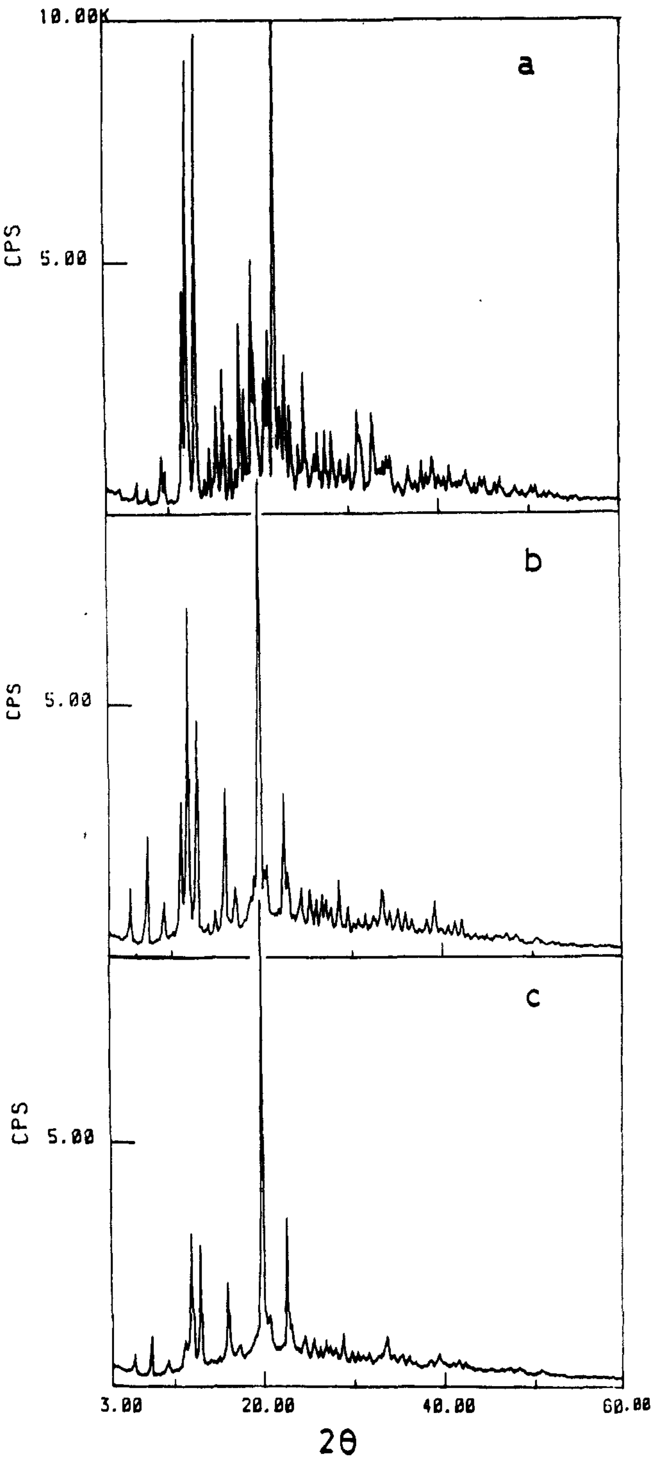

Figure 2. X-ray powder patterns of the complex of α-CD and propionic acid (a), that of α-CD and valeric acid (b), and that of α-CD and PEG (MW = 1000) (c). Wavelength of X-rays is 1.54 Å.

figure clearly shows that PEG of molecular weight 1000 precipitates most rapidly. The rates decrease as the molecular weight increases when the molecular weight is more than 1000. This may be partly due to the fact that the number of end groups decreases as the molecular weight increases.

The complex formation of α-CD with PEG was studied quantitatively. The amounts of the complex formed increased with the increase of PEG added to the aqueous solution of α-CD, and saturation was observed, indicating stoichiometric complexation. The saturation values show that more than 90% of the α-CD was consumed by complex formation with PEG.[6] From the initial slope, two ethylene glycol units were found to be bound in each α-CD cavity. The stoichiometries were further confirmed by the ^{1}H NMR spectrum. The length of two ethylene glycol units corresponds to the depth of the α-CD cavity (~7 Å).

The complexes can be dissolved in water by heating. The addition of an excess amount of benzoic acid, which is thought to be a competitive inhibitor,[7] to the suspension of the complex resulted in solubilization of the complex when the molecular weight of PEG was low (1000). The formation of the complex is evidently reversible.

The complexes were isolated by filtration or centrifugation, washed, and dried. The inclusion complexes are thermally stable. The decomposition points of the complexes are a little higher than that of each component. Thermogravimetric analysis shows that they decompose above 300 °C, although α-CD melts and decomposes below 300 °C. Poly(ethylene glycol) stabilizes α-CD.

Figure 2 shows the X-ray powder patterns of the complex of α-CD with PEG and with other low molecular weight compounds. The X-ray powder pattern shows that the complexes are crystalline,[8] and the patterns are very similar to those of the complex of α-CD with valeric acid or octanol, which have been reported to have extended column structure,[9] and totally different from those of the complexes with small molecules, such as propionic acid or propanol, which have a cage structure. These results indicate that the complexes of α-CD and PEG are isomorphous with those of channel-type structure rather than the so-called "cage" type structure.

Molecular model studies show that PEG chains are able to penetrate α-CD cavities, while the poly(propylene glycol) chain cannot pass through the α-CD cavity due to the hindrance of the methyl group on the main chain. These views are in accordance with our results that α-CD formed complexes with PEG but not with poly(propylene glycol). β-CD did not form complexes with PEG. The β-CD cavity is too large to fit a PEG chain. Model studies further indicate that the single cavity accommodates two ethylene glycol units.

PEG carrying bulky substituents such as the 3,5-dinitrobenzoyl group and 2,4-dinitrophenyl group at both ends of the PEG, which do not fit or pass through the α-CD cavity,[10] cannot give any complexes with α-CD.

In conclusion α-cyclodextrin forms complexes with poly(ethylene glycol) of various molecular weights to give crystalline complexes in high yields, although β-CD did not form complexes with PEG. Studies on the detailed structure of the complex are now in progress.

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Akira Harada* and Mikiharu Kamachi*

Department of Macromolecular Science
Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

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On a Controversy about Interpretation of Nuclear Magnetic Resonance Observations in Poly(dimethylsiloxane) Networks Cross-Linked in Solution

The use of deuteron magnetic resonance (^{2}H NMR) to study chain segment orientation in strained rubbers has increased in recent years.[1-4] Three years ago we published results concerning segmental orientation in elongated poly(dimethylsiloxane) (PDMS) networks prepared by an end-linking reaction in solution at different precursor polymer volume fractions, V_{2c}.[5] The experiments were performed either on deuterated solvent molecules used as NMR probes of unlabeled networks or directly on deuterated networks. In both cases we observed that, for a given elongation ratio, α, the segmental degree of order, S (related to the quadrupolar splitting $\Delta\nu$), increases with increasing values of the concentration, V_{2c}, the molecular weight of the precursor chains being held constant. This dependence of S was suggested to be related to an increase of chain entanglements trapped during the end-linking reaction carried out at high V_{2c}. Cooperative diffusion constant measurements by light scattering on polystyrene[6] and PDMS[7] networks, swelling and elastic properties of PDMS networks,[8] elasticity measurements on polyurethane networks[9] and NMR studies of the swelling process of PDMS networks[10] all support this interpretation.

Recently this interpretation was considered "erroneous" by Erman and Mark.[11] These authors argued that the observed effects are only due to the fact that the reference volume of the network during cross-linking is different from its volume during the NMR experiments. They reinterpreted our results in terms of the polymer volume fractions V_2 (during NMR experiments performed on dry samples, i.e., $V_2 = 1$) and V_{2c} (during cross-linking) so that the observed behavior of the segmental order, S, would be attributed to the so-called "memory term", $(V_{2c}/V_2)^{2/3}$, as indicated in relation 7 of the ref 11.

In our opinion, one cannot be totally categorical concerning the existence and the role of the "memory term". To the best of our knowledge to date, there are no decisive experiments showing that chains are "supercontracted" when $V_2 > V_{2c}$. We may also add that no influence of cross-linking on the chain dimensions has been detected; in particular, small-angle neutron scattering experiments carried out on dry networks prepared at different concentrations V_{2c} have not revealed any influence of V_{2c} on the chain dimensions, while the Young modulus was noticeably affected.[12] Moreover, various experiments do not lead to the expected V_{2c} dependence resulting from the "memory effect". For instance, it is found that the polymer volume fraction at swelling equilibrium[8] goes like $V_{2c}^{3/4}$, while the expected dependence would be $V_{2c}^{2/5}$. Also, the shear modulus of dry PDMS networks[13,14] does not scale as the expected law $V_{2c}^{2/3}$. However, the main purpose of this note is to show that, even if such a "memory term" does exist, this effect is not sufficient to explain all the NMR results reported in ref 5.

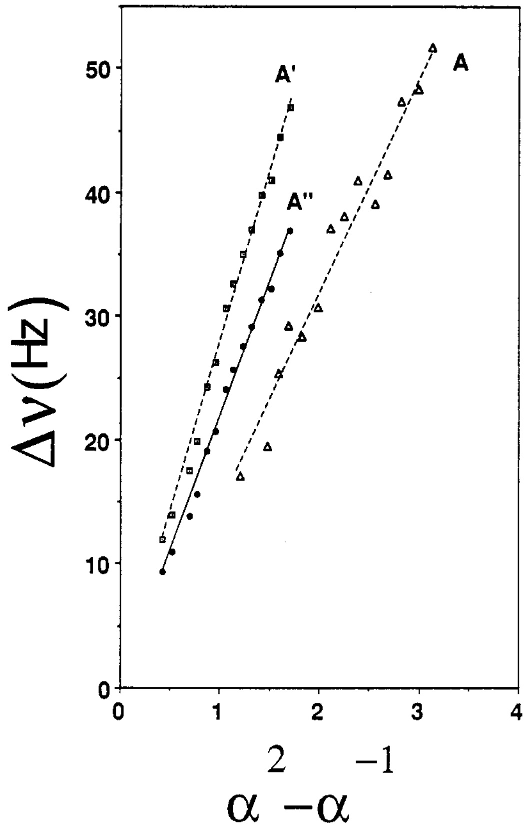

Figure 1. Quadrupolar splitting $\Delta\nu$ vs $\alpha^2 - \alpha^{-1}$ for two end-linked PDMS networks (M_n = 25 000) synthesized in the dry state (sample A′) and in solution at a concentration V_{2c} = 0.7 (sample A); these data have already been reported in Figure 3 of ref 5. The full line (A″) is obtained by multiplying the experimental data of curve A′ by the "memory term" $(V_{2c}/V_2)^{2/3}$ = 0.79. The elongation ratio, α, is relative to the unstretched volume V_2 during the NMR experiments.

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