The results of the thermal stability of polystyrenes with a maximum degradation temperature of nearly 400 °C were consistent with statements in our recent papers that the H-H and H-T linkages are of comparative stability as long as the fourth substituent on the carbon atom is a hydrogen atom. If the group is different, then the thermal stability of the H-H linkage is lower. A more detailed study of the degradation behavior of H-H polystyrene and the determination of several mechanical properties will be the subject of a separate paper.

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Polymerization of Cadmium Octadecylfumarate in Multilayers

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ABSTRACT: The UV-initiated polyreaction of Langmuir–Blodgett multilayers of cadmium octadecylfumarate was studied. For structural comparison the dimensions of the monoclinic unit cell of crystalline monomeric material were determined. The structure of the multilayers was characterized by x-ray and electron diffraction. Approximately the first ten layers showed hexagonal packing of the monomer molecules with the paraffin chains perpendicular on the support, whereas in thicker layers partial rearrangement occurred to the monoclinic modification. The monoclinic crystallites are arranged in three preferred directions, resulting from the original hexagonal symmetry. (Orientation of the monomer molecules was further characterized by infrared spectra.) Both modifications can be polymerized by UV light, the resulting polymer structure being the same in both cases. In the case of the monoclinic phase at approximately 40% conversion a phase transition monomer to polymer occurs. The kinetics of the reaction was followed by UV spectroscopy. By polymerization of alternating cadmium octadecylfumarate/cadmium stearate multilayers it could be shown that the reaction occurs independently from the nature of the neighboring layer in a separate plane.

In the last few years, first studies have been made of polyreactions in Langmuir–Blodgett multilayers (or "built-up monomolecular films").[2-5] The monomeric multilayers can be built up from monomolecular layers of the monomer on the gas/water interface by multiple deposition onto a solid support.[6,7] These multilayers can be polymerized to ultrathin polymer layers of controlled thickness. Their potential interest lies among other things in the increased mechanical stability in comparison to low molecular weight multilayers.

Concerning the building up of monomer multilayers, the question arises if the orientation of the molecules on the water surface is preserved during deposition or if new structures are formed. Second, it must be established if and how monomer orientation and layered structure change during the polyreaction.

Experimental Section

Materials. Commercial octadecylhydrogenfumarate was recrystallized several times from methanol, mp = 94 °C. The cadmium salt was prepared by shaking a solution of 6 g of octadecylhydrogenfumarate in 500 mL of chloroform with a solution of 9 g of cadmium acetate in 500 mL of water. The cadmium salt precipitates at the interface. After washing with water, methanol, and chloroform the raw product was recrystallized from a mixture of water/dioxane/chloroform. This mixture was also used for the preparation of a single crystal; the saturated solution (40 °C) was cooled at a rate of 0.5 °C/h.

The water, used as the monolayer substrate, was distilled twice (100- and 50-cm column), the first time from alkaline permanganate solution. The chloroform for spreading was analytical grade and was checked for surface active impurities.

The plates, onto which the multilayers were deposited (quartz Suprasil I for UV spectroscopy and diffraction studies and Germanium for IR spectroscopy), were cleaned in a plasma cleaner (Harrick, Ossining, N.Y.).

Procedures. The Langmuir trough used for building up the multilayers was of the type as described by Kuhn et al.[8] Surface pressure was kept constant by calibrated weights via a pulley system and floating barrier. A 2×10^{-3} M solution of the monomer in chloroform was spread on a 2×10^{-4} M solution of cadmium chloride in water. All multilayers were deposited at a constant surface pressure of 30 dyn/cm with a dipping speed of less than 1 mm/s. At 30 dyn/cm a monomer molecule occupies an area of 20 Å^2. In all cases a deposition was observed during the downward trip of the plate as well as during the upward trip. This means a Y deposition of the layers, though this does not necessarily result in a Y structure (i.e., tail-head, head-tail arrangement of the molecules).

A detailed description of the Langmuir trough for building alternating multilayers can be found in a previous publication.[2b] Basically the apparatus consists of two troughs which are connected by a double gated canal for moving the deposition plates under water from one trough to the other. The gates prevent the mixing of the two monolayers.

The polymerization of the multilayers was initiated by UV irradiation with a high-pressure mercury lamp (Osram HBO 200).

The UV spectra of the multilayers were recorded on a Cary-14 spectrometer.

Fourier transform infrared spectra were taken with a Digilab FTS-14 spectrometer.

X-ray diffraction pictures were recorded with a Siemens Kristalloflex-4 and Ni-filtered Cu Kα radiation. A countertube goniometer was used for powder diagrams and multilayer pictures and a Weissenberg camera was used for single-crystal investigation.

To take electron diffraction pictures in the electron microscope, the multilayers had to be transferred onto small copper grids. For this purpose, a multilayer covered quartz plate was dipped obliquely and very slowly through a clean water surface. The water penetrated between the multilayers and the quartz plate causing the multilayer package to float off onto the water surface. The layers were then picked up with a copper grid from the water surface for the electron diffraction investigation. For calibration of the microscope TlCl was used. For the preparation of the replicas, the multilayers were shadowed on their support with carbon/platinum. Then the multilayers together with the carbon/platinum film were removed from the support as described before and picked up with a copper grid. Finally, the multilayer material was removed from the grid with chloroform leaving only the carbon/platinum replica.

Results and Discussion

Monolayers of octadecylhydrogenfumarate were spread on cadmium chloride solution and transferred onto the plates according to the Langmuir–Blodgett technique as described in the experimental part.

First it was checked whether the salt had been formed or if acid also was transferred. For this purpose, germanium plates were chosen as a support and transmission infrared spectra were taken with a Fourier-Transform spectrometer. A spectrum of 2×25 layers is shown in Figure 1.

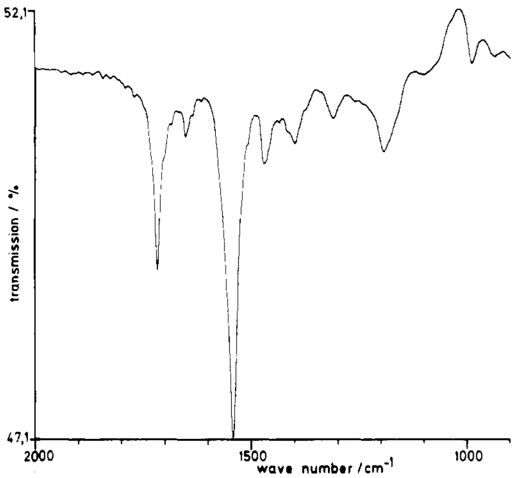

Figure 1. Infrared spectrum of 2×25 layers of cadmium octadecylfumarate on germanium. Transmission spectrum with Fourier-Transform instrument. Average of 200 spectra.

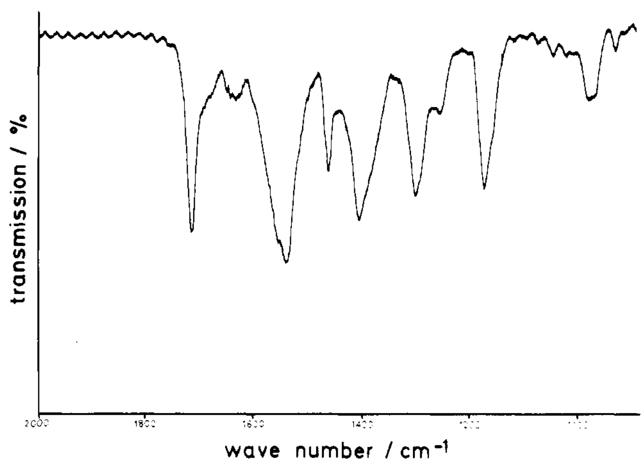

Figure 2. Infrared spectrum of cadmium octadecylfumarate (KBr pellet).

A comparison of the spectrum in Figure 1 with the spectrum of bulk octadecylhydrogenfumarate (not shown) and its cadmium salt (Figure 2) proves that the multilayers contain only salt (CO_2^- stretch at 1545 cm^{-1}). The sensitivity of the Fourier technique and the multiple scanning and subtraction possibilities of the computer system allows one to get a transmission spectrum of a single layer, also consisting of the cadmium salt. It is evident that the two spectra differ in the intensities of some bands; particularly the 1300-cm^{-1} (*trans*-vinyl C–H bend), 1410-cm^{-1}, and 1465 cm^{-1} (paraffin C–H bend) bands of the multilayer spectrum show relative low extinction. As the infrared beam is directed perpendicular to the plane of the multilayers, the electric vector lies in the layer plane, meaning that any vibration with a transition moment in this plane will show a high extinction and vice versa. As the 1300-cm^{-1} band is attributed to a C–H bend vibration, the small extinction must be interpreted such that the vinyl C–H bond lies more or less in the layer plane. A similar interpretation is suggested for the relative low intensity of the 1465-cm^{-1} band. This means that the paraffin chains are close to perpendicular to the layer plane (further work, described below, shows that approximately the first 10 layers have side chains perpendicular to the layer plane and subsequent layers have side chains at an angle of 37° from the perpendicular).

The next task was to establish the structure of the multilayers and to check if an aging, as described in the literature,[9-17] could be observed. In order to compare the multilayer structure with the structure of the crystalline cadmium octadecylfumarate, the unit cell of the latter was determined. From powder diagrams and Weissenberg pictures of a single crystal, the following values were obtained: monoclinic unit cell with $a = 23.1$, $b = 5.1$, $c = 53.8$ Å and $\beta = 127°$. This gives a layer spacing of 43.0 Å, which is the direction of the c^* axis in reciprical space. Thus the c axis (side-chain axis) is inclined 37° to the perpendicular. Oscillation pictures of 200 aged layers on a microscope cover slide gave the same 001 spacing of 43 Å, the planes being parallel to the support. This means that in this already rather thick multilayer the same structure was present as in the crystalline material. As all layers are parallel to the plane of the supporting plate, the multilayer in this direction has single-crystal character. As a consequence

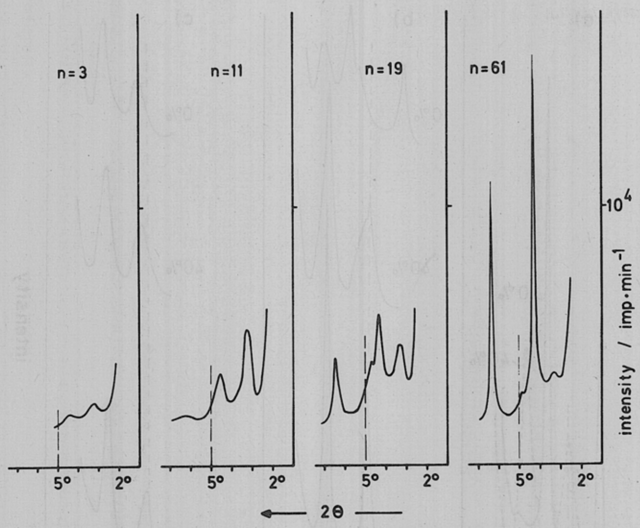

Figure 3. Counter-tube goniometer tracing of n layers of cadmium octadecylfumarate on quartz; Cu Kα radiation.

all 00l planes and no others are in reflecting position if a multilayer covered plate is mounted in the sample holder of a x-ray counter-tube powder goniometer. Together with the high diffracting power of the cadmium ions, it should be possible to get 00l reflections of very thin multilayer samples. Figure 3 shows such 00l reflections of n = 3, 11, 19, and 61 layers.

The 00l spacing of the thickest (n = 61) multilayer corresponds to 43 Å, which is the monoclinic layer spacing as already found with oscillation pictures. But there are two more very weak reflections with a spacing of 58 Å. In the samples with less layers this peak becomes more dominant, and at a layer thickness of 11 and less this is the only spacing observed. As the length of the molecule is estimated to be approximately 30 Å, this means that in thin multilayers the molecules are standing upright on the layer plane, forming a Y structure (head, tail-tail, head). Phase transformation within these multilayers could not be observed, even after storage for half a year at room temperature. In thicker layers both modifications are present in the same multilayer.

Electron Diffraction and Microscopy. With the x-ray technique used, only the large layer spacing (i.e., d_{00l}) could be determined. For a further insight into the packing of the molecules electron diffraction pictures were taken in an electron microscope, with the electron beam perpendicular to the layer plane. The preparation of the samples has been described above. Figure 4 shows the diffraction pictures of 1, 11, and 21 layers, the d values for the first two being 4.2 Å.

This spacing, together with the hexagonal symmetry, is in agreement with the above statement that in thin multilayers the paraffin chains are standing upright on the layer plane in a quasihexagonal packing. As the pictures were taken far below the melting point, the hexagonal pattern is probably not due to a high-temperature rotary phase but to an order–disorder structure, stabilized by surface forces. Figure 4c still shows hexagonal symmetry but with a multiplicity of diffraction arcs. The x-ray results suggest that this is due to the presence of the monoclinic phase. The hexagonal symmetry can be interpreted as follows: primarily the multilayers are deposited in the hexagonal arrangement and during the following phase change, the monoclinic crystallites are oriented relative to the axes of the original lattice. The superposition of the diffraction of these crystallites will result in a diffraction picture with hexagonal symmetry. The reflections were indexed with the aid of the known monoclinic unit cell (Table I).

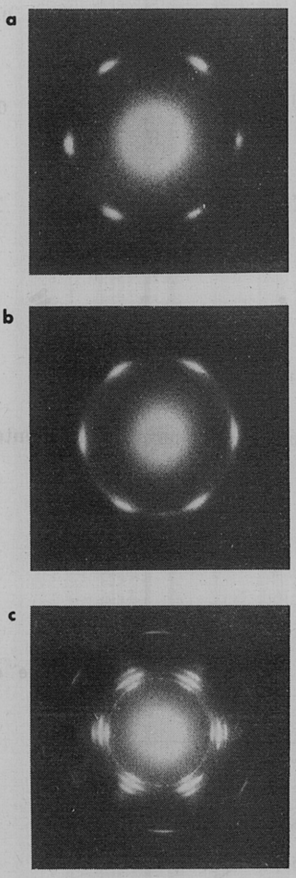

Figure 4. Electron-diffraction pictures of (a) 1, (b) 11, and (c) 21 layers of cadmium octadecylfumarate.

Table I
Indexing of the Strongest Reflections, Obtained by Electron Diffraction on a Multilayer of 21 Layers of Cadmium Octadecylfumarate[a]

hkl	d^*, Å^{-1}	d^*_{calcd}, Å^{-1}
010	0.21	0.198
213	0.21	0.215
314[b]	0.24	0.237
608	0.26	0.261
020	0.40	0.396

[a] d^*_{calcd} from dimensions of monoclinic unit cell. [b] Probably superimposed by 100 reflection of hexagonal phase of monomer or of polymer formed under electron irradiation.

The superposition of monoclinic diffraction patterns to form a hexagonal symmetry is shown schematically in Figure 5.

As the crystallites are oriented relative to the layer plane, not all lattice planes should be in reflecting position. As the layer plane is perpendicular to the electron beam, the hk0 reflections should not be observed because of the monoclinic angle of β = 127°, as can be seen from Figure 6. On the other hand 2k3, 3k4, and 6k8 reflections should be on the sphere of reflection assuming a reasonable spot size, in addition to 0k0 reflections.

Polymerization Experiments. The multilayer samples were fully polymerized by irradiation with UV light. The reaction can be followed by observation of the change in UV absorption at the absorption maximum of the monomer at 210 nm (Figure 7).

During UV irradiation of other fumaric acid derivatives dimerization[18] as well as polymerization[19a] had been observed. The ATR (attenuated total reflectance) infrared spectrum of the irradiated multilayer shows a disappearance of the double

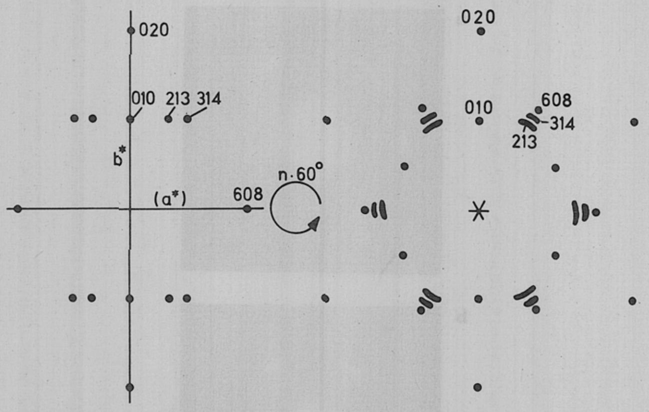

Figure 5. Superimposition of hexagonally oriented diffraction pictures.

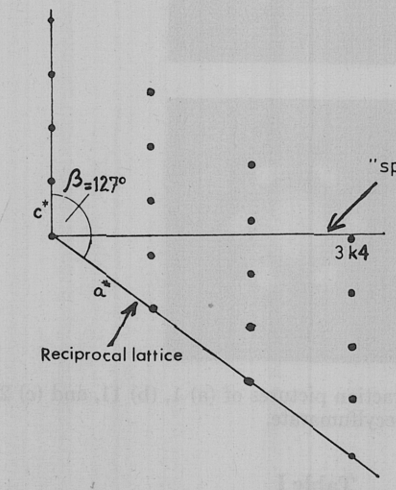

Figure 6. Diffraction of an electron beam directed perpendicular to the layer plane of a monoclinic cadmium octadecylfumarate crystal.

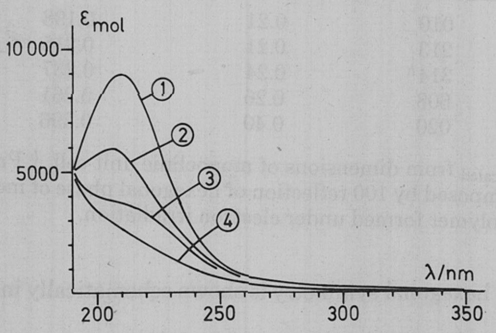

Figure 7. UV spectra of a cadmium octadecylfumarate multilayer after UV irradiation for 0 (one), 1 (two), 3 (three), and 100 h (four).

bond (975, 1300 cm^{-1}) and a broadening of the remaining bands. The product was further analyzed by slow pyrolysis in the ion source of a mass spectrometer.[19b] At temperatures below 400 °C the fission of the hydrocarbon side chains was observed, probably with formation of anhydride structures.[20] Around 400 °C fragmentation of the main chain occurs. The observed fragments (*m/e* 207, 429) correspond to trimers and higher. Dimers could not be observed. From all this evidence it was concluded that the product was in fact a poly(cadmium octadecylfumarate).

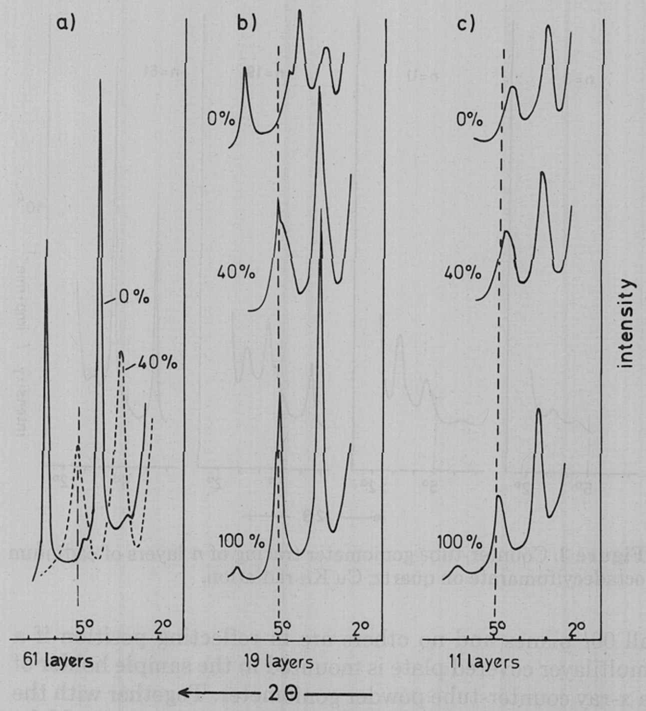

Figure 8. 001 reflections during polymerization of cadmium octadecylfumarate in multilayers (Cu Kα radiation, countertube goniometer arrangement): (a) 61 layers, (b) 19 layers, and (c) 11 layers. Percentages refer to conversion.

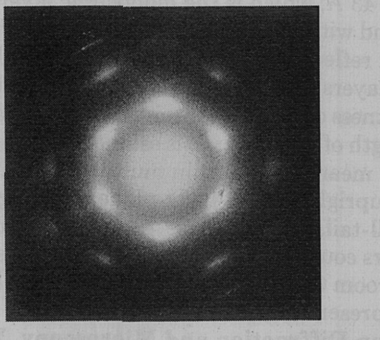

Figure 9. Electron diffraction picture of a poly(cadmium octadecylfumarate) multilayer ($n = 21$).

Structural Changes during Polymerization. X-ray tracings of polymerized multilayers were recorded in the same goniometer arrangement as described above. The reflections were less sharp than those of the monomer and correspond to a layer spacing of 55 Å, independent of the number of layers (Figure 8).

This means that the paraffin chains of the monoclinic phase *become erect during the reaction. Electron diffraction pictures* of the polymer show a diffuse hexagonal pattern with a spacing of 4.2 Å (Figure 9).

These two features, the long spacing of approximately twice the length of the monomer molecule and the quasihexagonal packing of the paraffin chains, are typical of comblike polymers with long paraffin side chains.[21,22] These results therefore lend further support to the assumption of a polymeric product.

Following the layer spacing during the polymerization process, thin and thick multilayers behave differently (Figure 8). For thin layers there is a gradual change from monomer spacing to polymer spacing, whereas in thick layers with mainly monoclinic structure there is a sudden change from monomer spacing to polymer spacing at approximately 40% conversion. A similar phase change has been observed during the polymerization of vinyl stearate in the solid state.[23]

If the two monomeric phases are present (Figure 8b), a superposition of the latter two cases is observed.

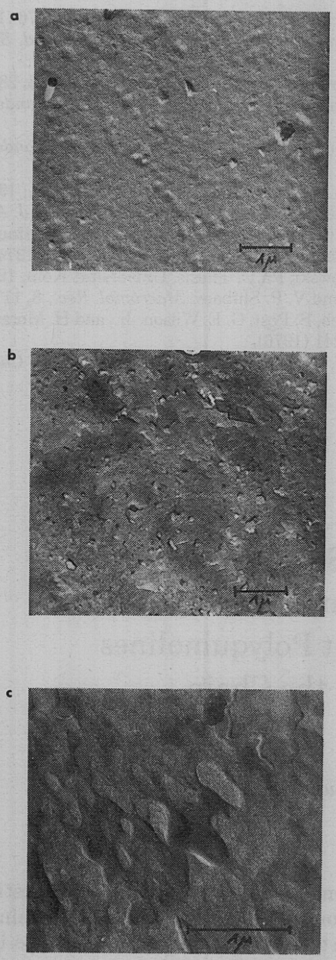

Figure 10. Replicas (carbon/platinum shadowed) of (a) 11 and (b) 21 monomeric layers of cadmium octadecylfumarate. (c) The same as b but polymerized.

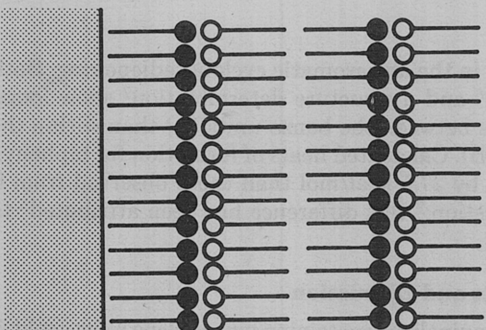

Figure 11. Structure of an alternating Y layer: (○) cadmium stearate, (●) cadmium octadecylfumarate.

These differences are also seen in replicas from multilayers, which are still on their support (Figure 10). The thin layer ($n = 11$) has a nearly even surface, while in the thicker ($n = 21$) monomeric layer crystallites can be seen. The polymerized sample (Figure 10c) also shows a more or less even surface.

One can summarize that in multilayers of cadmium octadecylfumarate two different phases can exist, their appearance depending on the thickness of the multilayer, although it is clear that the monoclinic phase developed from the original hexagonal phase. It is not clear why the first 10 or 11 layers do not undergo this phase change. Both phases have Y structure (head, tail-tail, head) and differ in the angle of tilt of the paraffin chain. They both can be photopolymerized to a polymer with preservation of the layer planes. The structure of the polymer layers seems to be independent of their origin. It appears that a solid solution of monomer and polymer side chains occurs at all conversions during the polymerization of the hexagonal monomer, while during the polymerization of the monoclinic monomer a solid solution of polymer side chains in the monomer structure persists until about 40% conversion which converts above that conversion to a solid solution similar to that of the former case.

Polymerization in Alternating Multilayers. The question then arises as to what degree the polymerization process is accompanied by local rearrangement or melting; second, does the polymerization occur within a separate layer plane or does it involve two neighboring layers, perhaps in a kind of zig-zag reaction process. This question can be answered when two polymerizable layers are separated by an inert layer of, e.g., cadmium stearate. The apparatus used for preparing alternating layers had been described in the literature before.[2b] Figure 11 shows schematically the structure of such a layer.

The structure of the alternating multilayer was checked by x-ray diffraction: the pure cadmium stearate layer has a spacing of 58 Å and the alternating layer (six double layers) has a spacing of 54 Å. An interdiffusion or phase segragation can consequently be excluded. The quasihexagonal structure, as was found for thin cadmium octadecylfumarate layers, is still existent in an alternating layer and is not disturbed by the presence of the cadmium stearate layers.

These alternating layers were now irradiated with the same UV intensity as used before and the reaction was followed by recording the change in UV absorption. At the same time a pure cadmium octadecylfumarate multilayer was irradiated as a reference. Within the limits of experimental error no difference in reactivity could be detected. This means that the reaction must occur within a single-layer plane, independent of the neighboring layers. This can be interpreted as a topochemical effect of the structure of a separate layer. The resulting poly(cadmium octadecylfumarate)/cadmium stearate multilayer has a long spacing of 53 Å.

Conclusions

(1) Cadmium octadecylfumarate is suitable for building up Langmuir–Blodgett multilayers, the structure of which is dependent on the number of layers deposited: thin layers show a hexagonal structure, thicker layers show additionally the regular monoclinic structure, as observed in the bulk crystal. The monoclinic crystallites are arranged in a hexagonal symmetry resulting from a phase transition from the original hexagonal phase.

(2) A polymerization reaction can be initiated in these layers by UV irradiation.

(3) It appears that a solid solution of monomer and polymer side chains occurs at all conversions during the polymerization of the hexagonal monomer, while during the polymerization of the monoclinic monomer a solid solution of polymer side chains in the monomer structure persists until about 40% conversion, which converts above that conversion to a solid solution similar to that of the former case.

(4) The reaction occurs in all cases in a separate layer plane, independent of the neighboring layers, as could be shown by polymerization experiments with alternating layers.

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Biphenylene as a Cross-Linking Site. Curing Conditions, Glass Transition Temperatures, and Moduli of High Molecular Weight Polyquinolines Containing Biphenylene Units in the Chain

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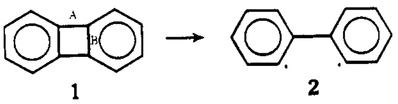
ABSTRACT: A series of polyquinolines containing biphenylene units in the main chain were prepared by substituting 2,6-diacetylbiphenylene for 4,4′-diacetyldiphenyl ether in polymerizations with 3,3′-dibenzoyl-4,4′-diaminodiphenyl ether. As the incorporation of biphenylene units increased, T_g and the temperature for the onset of cross-linking by opening of the biphenylene ring increased. Cross-linking takes place only above T_g and the onset of cross-linking parallels T_g of the polymer sample. Cross-linked polymers are characterized by higher T_g's, or disappearance of the T_g, and higher moduli both below and above T_g. The higher degree of cross-linking obtained from polymers containing higher incorporation of biphenylene resulted in higher moduli. Rhodium catalyzed the cross-linking reaction, allowing lower curing temperatures and shorter times.

The incorporation of biphenylene into thermally stable, totally aromatic polymers, such as polyquinolines, affords an attractive method of cross-linking these thermally stable materials that have proven to be difficult to cure.[1,2] The cross-linking reaction takes place at convenient temperatures, no volatiles are formed, and the structures produced are thermally stable.

Biphenylene (**1**) undergoes thermolysis at ~400 °C and, depending on the reaction conditions, yields tetrabenzocyclooctatraene, polymer, or biphenyl, resulting from radical abstraction of hydrogen from solvent.[3,4] Although the structure of the polymer was not determined, it likely contains poly(*o*-phenylene) segments. These reports suggest a diradical (**2**) as the reactive intermediate in pyrolysis. Thus, any structure formed as a result of the thermolysis of a biphenylene unit in a thermally stable polymer would be expected to maintain the high-temperature structural integrity of the polymer.



1 **2**

SCF–MO calculations suggest[5] that biphenylene is antiaromatic and should be somewhat chemically unstable, undergoing reactions which would disrupt the conjugative effects in the antiaromatic cyclobutadiene ring. Both calculations[6] and a structure determination[7] show longer bond lengths between the benzo units (A) than within the benzo units (B). Calculated heats of formation for biphenylene are higher by 27.5 kcal/mol than those observed from heats of combustion;[7] this difference has been attributed[5] to strain energy.

Results and Discussion

Polyquinolines containing biphenylene units could be cured thermally at temperatues (300–350 °C) somewhat lower than those known to effect thermolysis of biphenylene.[3,4] In an effort to lower the temperature and reduce the time necessary for curing, we had carried out the reaction in the presence of norbornadienechlororhodium dimer **3**. Although the rhodium catalyst decreased the curing time, it was necessary in all cases to heat the sample above the glass transition temperature of the polymer in order to effect cross-linking.

Although rhodium catalysts are known to open strained cyclic hydrocarbons by an oxidative addition mechanism,[8] the products of the rhodium catalyzed reaction of biphenylene were unknown. Pryolysis of biphenylene containing a catalytic amount of the rhodium catalyst at 200 °C produced dibenzocyclooctatetraene in a 44% yield (recrystallized) and polymer. Thus, the products of the catalyzed reaction are the same as those obtained from the uncatalyzed thermolysis. By analogy to the cubane reaction,[8] however, it might be expected that benzyne is the reactive intermediate. This reaction,

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