Radiation-Induced Polymerization of Octadecyl Acrylate at a Nitrogen–Water Interface under Constant Surface Pressure Conditions[1]

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ABSTRACT: Studies have been carried out in an attempt to elucidate the reactivity of monomer in relation to the orientation of monomer molecules in a monolayer. An octadecyl acrylate monolayer was compressed to a desired surface pressure and then irradiated with an electron beam from a Van de Graaff electron accelerator in a nitrogen atmosphere. The reaction was followed by measuring the surface area change during irradiation and found to follow first-order kinetics. The rate of polymerization reached a maximum at a molecular area of 20.2 Å^2/molecule.

Several studies have been made on the polymerization of monolayers at a gas–water interface initiated by ultraviolet illumination or by a catalyst dissolved in the subphase or contained in the monolayer,[2–5] but little has been reported on that initiated by ionizing radiation. The radiation-induced polymerization of a monolayer at the interface is particularly suitable for studying the reactivity of monomer in relation to the arrangement of monomer molecules in radiation-induced solid-state polymerization where the monomer arrangement in the solid is an important factor, because the system may be regarded as a two-dimensional crystal and the molecular arrangement can be altered by varying the surface pressure. Another interest of this system lies in the initiation process of the polymerization in which the intermediates formed in the subphase by radiation diffuse up to the surface to react with the monomer monolayer.

In a previous report, we have shown that the octadecyl acrylate monolayer polymerizes effectively when exposed to electron beams from a Van de Graaff accelerator when the area of a nitrogen–water interface is held constant. However, the dependence of the rate of polymerization on the surface pressure which relates to the monomer arrangement in the monolayer was not determined, because the surface pressure change caused by radiation-induced surface polymerization was quite large under the constant surface area condition employed.

In this paper, we wish to report a study of the rate of polymerization of octadecyl acrylate (ODA) monolayers initiated by electron beam irradiation under a constant surface pressure condition in relation to the monomer arrangement in the monolayer.

Experimental Section

Apparatus. The apparatus used in the present study will be described briefly, since the details have been published elsewhere.[7] The apparatus is essentially a Langmuir trough which is modified for the constant surface pressure operation.

Any surface pressure change caused by surface chemical reaction is detected by a linear variable differential transformer, and converted to an electric signal which, after amplification by a servo amplifier, drives a servo motor that moves a barrier which changes the surface area and thereby compensates for the surface pressure change.

The surface pressure during irradiation was kept constant within 0.5 dyn/cm at an initial surface pressure which had been selected by applying appropriate bias voltage to the servo amplifier. During irradiation the surface reaction was followed by a surface area change which was recorded on a recorder as a function of time. The whole system was constructed in an aluminum container in which air was replaced with nitrogen.

Materials. Reagents, water, and solvents were the same as those described in the previous report. A benzene solution containing about 10 mg ODA/ml was used to spread the monomer on the water subphase which had been deaerated and blanketed with nitrogen before filling the trough. Ten minutes were allowed for evaporation of the solvent to form the monolayer before irradiation.

Poly(octadecyl acrylate) (PODA) of varying molecular weight used for reference in the analysis of irradiated film materials was prepared by solution polymerization with different concentrations of ODA and AIBN as catalyst at 84° for 24 hr in benzene. The polymers were purified by repeated dissolution in benzene followed by precipitation in methanol and drying *in vacuo*. The molecular weights of the polymers were determined by viscosity measurement and by the isopiestic method on a Perkin-Elmer molecular weight apparatus (type 11t) and the results are given in Table I along with R_f values obtained by thin layer chromatography.

Irradiation. Irradiations were carried out using an electron beam from a Van de Graaff accelerator (1.5 MeV, 20 μA, or beam scanning width 30 cm). The dose rate averaged over the water surface was 7.7 krads/sec for electron beams of 1.5 MeV, 20 μA, 30 cm, as measured by the cellulose triacetate film dosimetry method.[8] The temperature of the subphase was 23°.

Analysis of the Film. Analyses of the film were carried out using the ATR infrared spectroscopic technique and thin layer chromatography. The irradiated film was collected on a selenium arsenide prism and the ATR infrared spectra were recorded on a Shimadzu AR275 type infrared spectrometer. The film on the prism was then dissolved in benzene and the solution was concentrated to 0.1 ml and then applied on a thin layer chromatographic plate (Merck, silica gel 60, layer thickness, 0.25 mm, 5 cm × 20 cm), which was developed by 20 ml of mixed solvent of *n*-hexane, diethyl ether, and acetic acid (15:5:1 by volume) for about an hour at 22° followed by visualization by spraying with 30% perchloric acid and heating the plate in an oven at 140° for 20 min.

Results and Discussion

Table II gives the main features of the ATR infrared spectra of the films of ODA irradiated at the nitrogen–water interface (a) and at the air–water interface (b) along with those of ODA (c) and PODA (d).

Examination of the bands in the infrared spectra listed in Table II reveals that the spectrum of the ODA monolayer changed to the one (a) which is close to the spectrum (d) of PODA when irradiated at the nitrogen–water interface, while the spectrum of ODA monolayer did not change significantly [see spectrum b] when irradiated at the air–water interface. This indicates that the ODA monolayer polymerizes when it is irradiated in the nitrogen atmosphere. The extent of conversion to polymer was obtained by thin layer chromatography as illustrated by Figure 1 in which the chromatograms are given for the irradiated film at the nitrogen–water interface (a), at the air–water interface (b), and for a synthetic mixture of ODA and PODA (1:10) (c). The broad peak appearing in the chromatogram (a) is due to a polymer (78%)[9] but the R_f value of this spot is apparently smaller than that of the reference polymer (c) suggesting that the molecular weight of the surface polymerized polymer is higher than that obtained by solution

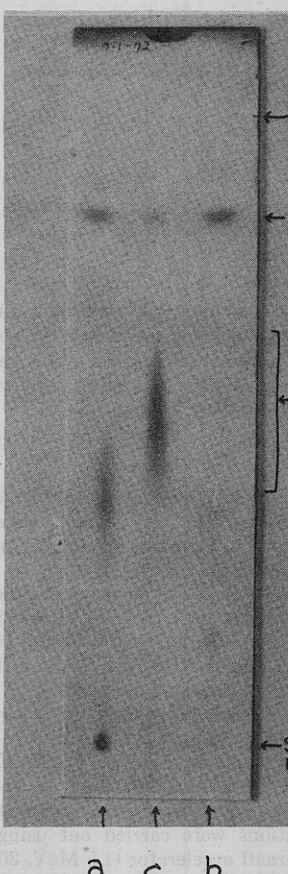

Figure 1. Typical thin layer chromatograms of the film substances: (a) ODA monolayer irradiated at the N_2–water interface, (b) at the air–water interface, and (c) synthetic 1:10 mixture of ODA and PODA-3.

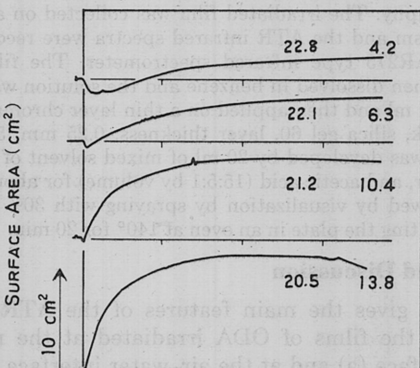

Figure 2. Surface area–time conversion curves for monolayer polymerizations at the nitrogen–water interface at different surface pressures. Initial molecular areas are also given.

polymerization ($\bar{M}_n \simeq 18{,}900$). The spot remaining at the starting point is probably due to cross-linked polymer (13%).[9] The chromatogram (b) obtained for ODA monolayer irradiated at the air–water interface shows no spot due to polymer but spots due to unreacted ODA monomer (88%)[9] and unidentified low molecular weight products.

Figure 2 shows that the surface area changes as a function of irradiation time at different surface pressures at the nitrogen–water interface. The surface area increased with irradiation time, leveled off, and then decreased. The increment of surface area is due to the polymerization of ODA monolayer, because analysis of the irradiated monolayer revealed that PODA is the main product.

Table I
Properties of PODA

	Concentration				
	Monomer, mol/l.	AIBN, mg/g	$[\eta]$	M_n	R_f
PODA-3	3.38×10^{-3}	0.615	0.118	18900	0.6
PODA-4	1.40×10^{-3}	0.652	0.145		0.57
Irradiated ODA monolayer at N_2–water interface					0.4

The initial decrease found in the rate curves at lower surface pressures is qualitatively consistent with an interaction of ODA and PODA which results in the surface pressure of ODA monolayer at a surface area around 22 Å²/molecule decreasing to a minimum and then increasing as the polymer content in the monolayer increases (see curve a in Figure 4, ref 10). The slow decrease after irradiation for 150 sec is probably due to radiolysis of the polymer film. The area change due to irradiation described above is consistent with the former observation on the irradiation effect on surface pressure at a constant interfacial area.

It is evident from Figure 2 that the surface area increased slowly at lower surface pressures, increased rapidly at medium pressures around 15 dyn/cm, and increased slowly at still higher surface pressures.

This fact can be explained as an effect of surface pressure on surface concentration and molecular orientation of the monomer in the monolayer. At lower surface pressures below the transition point, molecules are in a disordered state in the monolayer and the surface concentration of the molecules is low, and therefore the rate of propagation is also low.

An increase of surface pressure results in a more ordered state of the monolayer and in a higher monomer concentration. Both favor a molecular arrangement that increases the polymerization rate by bringing the double bonds in monomers closer to one another.

The decrease in rate at surface pressures above 15 dyn/cm may be due to the fact that the molecules are so closely packed that molecular motion, for example, rotation around an axis along the alkyl chain, becomes difficult. The polar groups are forced into a position above or below the original plane resulting in close contact between the paraffinic side chains and separation of the double bonds.

In order to obtain a clearer insight into the relation between the rate of polymerization and the surface pressure, it is necessary to estimate the rate constants from the area–time conversion curves recorded at different surface pressures.

A first-order plot of ln $(A_{ss} - A)$ against irradiation time is shown in Figure 3, where A_{ss} and A denote the surface area at steady state and at time t, respectively. The linear plot shows that the reaction follows first-order kinetics, if we assume that the area change is proportional to polymer conversion. This assumption is reasonable because no significant side reaction was found to occur in the analyses of the irradiated film, and an additivity rule is valid for most surface pressures except at low surface pressures (see Figure 2a in ref 10).

According to the above assumption, the surface concen-

Table II
ATR Infrared Spectra of Film Substances (cm^{-1})

Film substances	$\nu_{C=O}$	$\nu_{C=C}$	$\delta_{CH}{}^{CH_2}$	ν_{C-O-R}		$\delta_{CH}{}^{CH=CH_2}$	
(a) Irradiated ODA monolayer at the N_2–water interface	1735	No	1470	1250	1150	No	
(b) Irradiated ODA monolayer at the air–water interface	1742	1630	1470	1275	1190	1300	1410
(c) ODA monolayer	1728	1630	1470	1275	1190	1300	1410
(d) PODA monolayer	1742	No	1470	1250	1150	No	

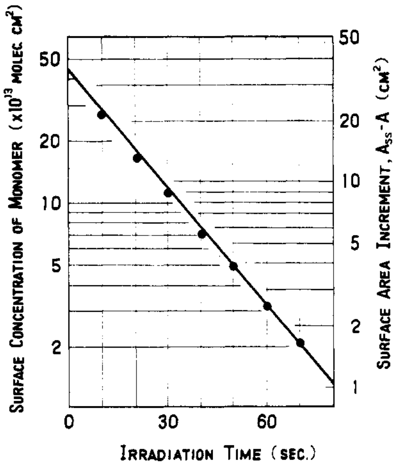

Figure 3. A first-order rate plot obtained from the time conversion curve obtained at 13.8 dyn/cm.

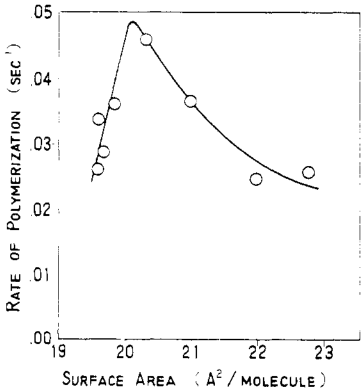

Figure 4. Rate of polymerization of ODA monolayers at the nitrogen-water interface as a function of molecular area.

tration of ODA [M] (molecules/cm^2) at time t (sec) was calculated by

$$[M] = \frac{A_0A_p - A_mA}{AA_m(A_p - A_m)} \times 10^{16}$$

where A_0 and A are the surface areas in cm^2 at irradiation time 0 and t, respectively, and A_m and A_p are the molecular areas obtained from the surface pressure–area curves of ODA and PODA in Å^2/molecule, respectively, at the surface pressure at which the rate curve was obtained. The resulting surface concentration [M] is given on the ordinate on the left of Figure 3.

The rate constants of the surface polymerization were calculated from the slope of the first-order plot and are shown in Figure 4 as a function of molecular area of ODA at the surface pressure studied. The rate constant apparently has an optimum value at 20.2 Å^2/molecule which is not very far from the cross-sectional area of a hydrocarbon chain calculated from crystalographical data reported for vinyl monomers having long alkyl chains.[11,12] This may be correlated with the fact that most vinyl monomers having long alkyl chains polymerize in the solid state at reasonable rates.[11-15]

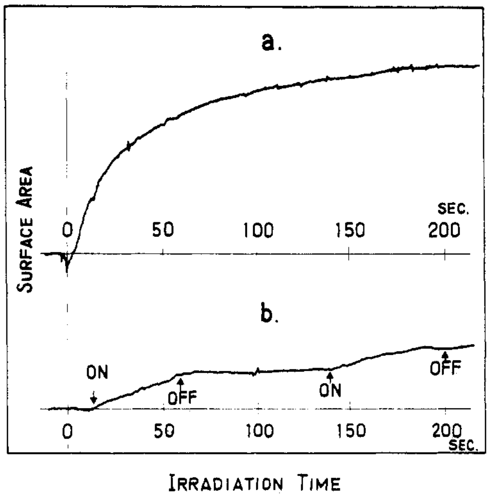

Figure 5. Surface area–time conversion curve for ODA monolayers: (a) on deaerated water containing 0.005 *M* KBr (dose rate 7.7 × 10^3 rads/sec), (b) on aerated water surface (dose rate, 1.8 × 10^4 rads/sec).

In order to investigate the contribution of radiation-produced intermediates in the aqueous subphase to the initiation process, the scavenger studies have been carried out using Br^- as a scavenger for OH· and O_2 for e^-. The results are given in Figures 5a and 5b, respectively. These additives did not produce any change in the surface pressure–area curve of ODA monolayer, indicating that there is no apparent interaction between the additives and ODA molecules on the surface. As is apparent from curve a in Figure 5, Br^- produced no effect on the conversion curve, while the rate was markedly reduced by the presence of O_2 regardless of the higher dose rate employed, as seen in curve b.

This result supports the possibility mentioned in a preliminary report[10] that the hydrated electron may initiate surface polymerization, but it does not exclude the possibility that oxygen simply inhibits the surface polymerization.

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Electron-Deficient Trisubstituted Olefins. A New Class of Reactive Comonomers

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ABSTRACT: Four electron-deficient trisubstituted ethylenes, tricyanoethylene (**5**), ethyl 2,3-dicyanoacrylate (**7**), dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**), and trimethyl ethylenetricarboxylate (**13**), copolymerized readily with monosubstituted electron-rich vinyl monomers under free-radical conditions. Monomer **13** was actually more reactive than methyl acrylate in copolymerization with styrene. Copolymer compositions were approximately 1:1. Best yields and molecular weights were obtained from **10** and **13**; side reactions presumably involving electron transfer caused lower yields and molecular weights from the extremely electrophilic **5** and **7**. Also, **10** and **13** gave alternating copolymers with *N*-vinylcarbazole, whereas **5** and **7** induced its cationic homopolymerization. In general, the most electron-rich comonomers gave highest yields, molecular weights, and rates of copolymerization. Electron-poor vinyl compounds such as methyl methacrylate did not copolymerize with the trisubstituted ethylenes. For steric reasons, no homopolymerizations or copolymerizations with electron-rich disubstituted olefins occurred. Charge-transfer complexes and spontaneous initiation were observed in many of these reactions. The copolymers exist as brittle glasses possessing high T_g values owing to conformational immobility and dipolar repulsion.

1,1-Disubstituted ethylenes are generally more reactive in free-radical polymerization than the monosubstituted olefins.[1,2] The intermediate radical is stabilized by resonance interaction with both substituents. Steric effects are not evident in reactivity, although they make themselves felt in low ceiling temperatures for the resulting polymers.

1,2-Disubstituted olefins, on the other hand, are markedly less reactive than the monosubstituted derivative. The β substituent gives no resonance stabilization and sterically hinders the attacking radical. Homopolymerization of 1,2-disubstituted olefins is difficult at best, and often impossible.[1,3] Their copolymerization is possible in two ways, however. A 1,2-disubstituted monomer will form random copolymers with a comonomer of similar polarity. As an example, dimethyl fumarate copolymerizes randomly with electron-deficient vinyl chloride.[4] On the other hand, comonomers of opposite polarity tend to give 1:1 alternating copolymers. Electron-poor maleic anhydride and electron-rich styrene give an altering copolymer.[5] Even a pair of 1,2-disubstituted monomers can copolymerize if they are of large, opposite polarities; the well-known copolymerization of maleic anhydride and stilbene is one example.[6] Polar interaction in the transition state overcomes the steric strain.

Few experimental investigations concerning the polymerization of trisubstituted olefins have been reported. This may reflect a belief that the steric effects encountered in the 1,2-disubstituted olefins would be worse for trisubstituted olefins. However, this should not be the case. The third substituent, located at the radical site, provides extra stabilization in the transition state, without any additional steric hindrance. Morever, if electron-withdrawing substituents such as cyano or carbomethoxy are involved, the extremely electron deficient double bond should be very susceptible to attack by electron-rich radicals. This analysis indicates that trisubstituted, electron-deficient olefins should copolymerize readily with electron-rich monomers to give alternating copolymers.

The small amount of data which we have found in the literature supports the view that a trisubstituted olefin can act as a free-radical monomer. Studies of the reactivity of several free radicals with the various chloroethylenes[7-9] indicated that trichloroethylene was as reactive toward an electron-rich polystyryl radical as was vinyl chloride (Table I). 1,1-Dicyano-2-phenylethylene and ethyl 1-cyano-2-phenylacrylate were more reactive toward styrene radicals than was *trans*-cinnamonitrile.[10]

In small amounts, these same compounds have also been shown to copolymerize with acrylonitrile,[11] as has α-cyanocinnamamide.[12]

Trisubstituted olefins carrying cyano and carboalkoxy groups are very electron-poor olefins which should copolymerize with electron-rich comonomers, leading to alternating copolymers with interesting and potentially useful properties. The first paper in this series briefly examined the copolymerization of tricyanoethylene (**5**) and ethyl 2,3-dicyanoacrylate (**7**) with styrene.[13] In this paper we have broadened this study to two other trisubstituted olefins, dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**) and trimethyl ethylenetricarboxylate (**13**), and to a wide variety of comonomers.