Monolayers of Linear Poly(vinyl Benzoate) and Its Mixtures with Stearic Acid

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Synopsis

Monomolecular films of linear poly(vinyl benzoate) (PVBz) and of mixtures of linear PVBz and stearic acid, show properties similar to branched PVBz and its mixtures with stearic acid. Nuclear magnetic resonance of linear and branched PVBz show no phenyl-hydrogen splitting, chemical shift, or other differences in relative peak positions. These results are consistent with the structure of PVBz as derived from general mechanistic considerations. The unusual monolayer properties of this polymer may be attributed to superior contiguous alignment of aromatic rings and tighter packing, but not to branching.

INTRODUCTION

Monomolecular film studies of poly(vinyl benzoate) (PVBz) prepared by free radical polymerization of the monomer vinyl benzoate have been reported by us.[1-3] The polymer shows unusual monolayer properties. It gives a very reproducible surface pressure–area isotherm with collapse unexpectedly high (53 dynes/cm.). The film is very rigid and has an unexpectedly small extrapolated area at zero pressure, (9 A.²/monomer unit). The average film thickness is about 20 A. These properties of poly(vinyl benzoate) are quite unlike those of related poly(vinyl esters),[2,4,5] poly-(methyl methacrylate),[6,7] or other horizontally oriented polymer monolayers at the water–air interface.[8]

It has been pointed out that vinyl benzoate is a self-inhibiting monomer, and on free radical-initiated polymerization can copolymerize with itself through the benzene ring.[9] The primary vinyl radicals can add to the aromatic ring to form a stabilized radical. In fact, the chain transfer constant of vinyl benzoate has been determined and is unusually high: 4×10^{-4}–6×10^{-4}.[10,11] This stabilized aromatic radical will then react in one of three ways: add fresh monomer and "copolymerize" through the aromatic ring, terminate with another primary polymer radical, or reform the aromatic nucleus and form a vinyl radical by donation of a hydrogen atom.[10] The first two events lead to a branched macromolecule. Proof of such branching in free radical-polymerized vinyl benzoate has been obtained by alkaline hydrolysis and reesterification of the polymer. A drop in the de-

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gree of polymerization is observed as shown by osmotic pressure and viscosity measurements of the polymer before and after the above treatment.[12]

Because of the unexpected properties of monolayers of branched poly(vinyl benzoate), an investigation of the isomeric linear polymer was undertaken.

EXPERIMENTAL

Linear Poly(vinyl Benzoate)

Poly(vinyl alcohol)(Matheson, Coleman, and Bell) was purified by three freeze-drying treatments from distilled water. It has a degree of polymerization of ~1700 as determined from viscosity measurement.[13] A 500-ml. three-necked flask was equipped with an efficient stirrer, reflux condenser, and dropping funnel. The apparatus was dried at 120°C. overnight and assembled in a dry box. The assembly was flushed with nitrogen, and 150 g. of purified pyridine was distilled directly into the flask. To this was added poly(vinyl alcohol) (13.2 g.) and the mixture heated while stirring to 60°C. and maintaining a nitrogen atmosphere until complete solution occurred. Benzoyl chloride (58 g.) was added dropwise to the clear solution at such a rate that the temperature would not rise above 65°C. After the addition had been completed, the reaction mixture was further stirred for 2.5 hr. at 65°C. It was then cooled, diluted with 400 ml. benzene, and the polymer was precipitated into excess methanol under vigorous agitation. After filtration and repeated washings with methanol, the polymer was redissolved in benzene and reprecipitated into methanol three times to remove traces of pyridine and pyridine hydrochloride. Final purification was made by freeze drying from a dilute benzene solution. The completeness of esterification was established by infrared and elemental analysis. The infrared absorption spectrum of the linear poly(vinyl benzoate) showed the disappearance of the 3 μ hydroxyl stretching vibration and the appearance of the strong carbonyl stretching vibration at 5.8 μ and the aromatic ester stretching vibrations at 7.9 and 9.1 μ. The viscosity-average molecular weight was ~250,000 from solutions in methyl ethyl ketone at 30°C.[14] Within experimental error, there was no evidence of any polymer degradation during benzoylation.

Branched poly(vinyl benzoate) was prepared as described by us previously.[1-3]

Surface Pressure–Area Measurements

The apparatus and techniques used to determine surface pressure–area isotherms have been discussed in detail previously.[15,16] A shallow, Teflon-coated trough was placed in a double walled incubator cabinet with thermopane front doors. The trough was filled with deionized water, twice redistilled in a quartz apparatus, and aerated with argon for at least 24 hr. The water had a pH of 6.7–6.9 and a specific resistance of 1.8–2.0 $\times$ 10^6

ohms.   The monolayer film was deposited on the water surface from a very dilute soution in benzene and was confined between a heavy moveable barrier on the one end and a float-torsion wire bridge on the other. The area was reduced in small decrements, and the corresponding angular deflection of a pointer connected to the bridge was determined.   From the latter, the surface pressure in dynes per centimeter was calculated.   All manipulations were made via controls mounted on the outside of the apparatus to prevent contamination from dust or extraneous surface active materials.   The whole assembly was leveed on a 500-lb. steel platform which rested on a vibration-free pad in the basement of the building.   These precautions helped insure excellent reproducibility.   Duplicate determinations from varying weights of substrate gave superimposable isotherms. Temperature was maintained constant at 24 ±0.2°C.

RESULTS AND DISCUSSION

The surface pressure–area isotherms for linear and branched poly(vinyl benzoate) of comparable degrees of polymerization are shown in Figure 1. The close similarity of the isotherms for the linear PVBz to that of the branched PVBz is striking.
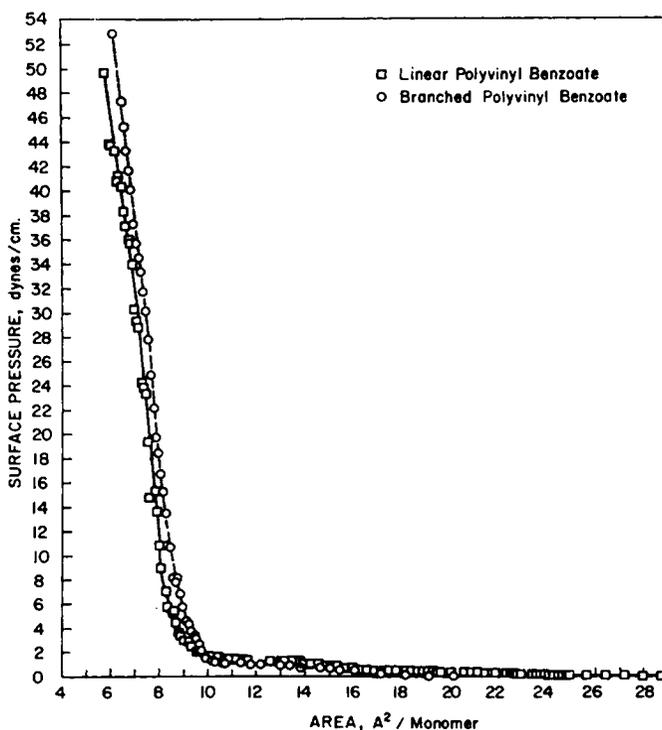

Fig. 1. Surface pressure–area isotherms for (□) linear and (O) branched poly(vinyl benzoate).
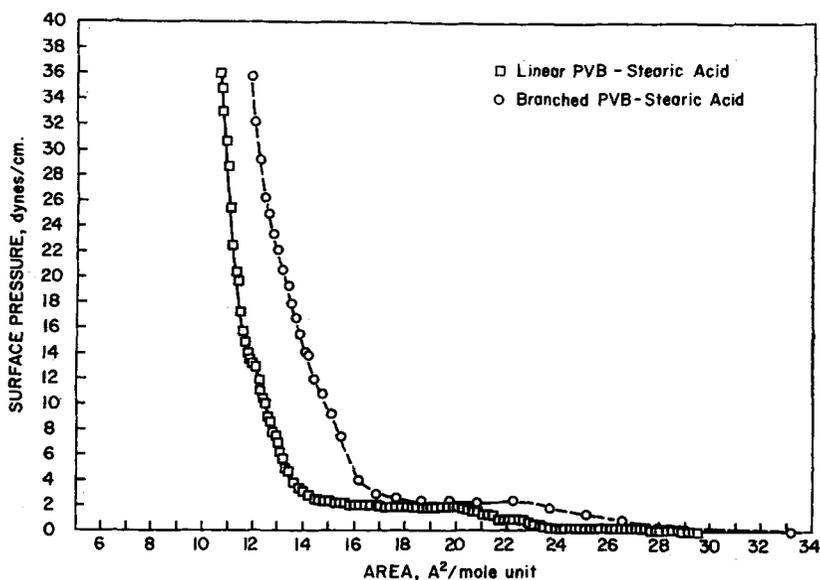
Fig. 2. Surface pressure-area isotherms for equiweight mixtures of poly(vinyl benzoates) and stearic acid: (□) linear PVB–stearic acid; (O) branched PVB–stearic acid.

Linear PVBz exhibits surface pressure at somewhat larger areas than does the branched polymer, i.e. about 24 A.^{2}/monomer unit versus 18 A.^{2}/monomer unit. The two isotherms are, however, almost superimposable at large areas and low pressure. The surface pressure of the linear polymer is consistently slightly higher than that of the branched material at areas of 20–10 A.^{2}/monomer unit. At areas smaller than 10 A.^{2}/monomer unit an inversion occurs, and the surface pressure of the branched polymer rises faster than that of the linear PVBz. At areas smaller than 10 A.^{2}/monomer unit the linear PVBz occupies somewhat smaller areas than does the branched polymer at identical surface pressures. Decrease of the available area to less than 10 A.^{2}/monomer unit brings about an abrupt rise in surface pressure for both polymers. Thus, surface pressure for the linear PVBz rises from about 1.7 dynes/cm. at 10 A.^{2}/monomer unit, to 50 dynes/cm. at collapse, due to a decrease of only a few square Angstroms/monomer unit in area. In this behavior the isotherm of the linear PVBz parallels closely that of the branched material. Collapse occurs at 50 dynes/cm., somewhat lower than the branched PVBz (53 dynes/cm.), but still unusually high for a horizontally oriented macromolecule. Poly(vinyl acetate) collapses at only 23 dynes/cm.[4,5] The steep and abrupt rise in pressure is more reminiscent of a vertically oriented molecule, like octadecylphosphonic or stearic acid.[3,16] The film of linear PVBz is very rigid and about as low in compressibility, (0.0066 cm./dyne), as the film of branched PVBz. The cross-sectional area of the linear PVBz film, at the extrapolated zero pressure, is only 8.8 A.^{2}/monomer unit, very close to that of the branched PVBz (9.0 A.^{2}/

monomer unit). The thickness of the linear PVBz film is similar to that of the branched PVBz film (~20 A.), assuming that the density of the film is identical to that of the bulk linear polymer. Film thickness values for PVBz monolayers have also been confirmed by an independent method of capacity measurements across two electrodes separated by the polymer film. Values of 10–20 nF./mm.^{2} were obtained. A film thickness of 20–25 A. was calculated assuming a dielectric constant of the order of 3 for PVBz.[17]

Because of the unusual properties of branched PVBz, we investigated the behavior of binary mixtures of the polymer and vertically oriented compound.[2,3] The pressure–area isotherm of an equiweight mixture of linear PVBz and stearic acid is now shown in Figure 2. For comparison, the isotherm of a similar mixture of branched PVBz and stearic acid is also given. The linear PVBz film alone exhibited surface pressure at somewhat larger areas than the branched polymer (Fig. 1). The linear PVBz–stearic acid mixture, compared to the branched PVBz–stearic acid mixture, shows the reverse effect. Surface pressure first commences at about 28 A.^{2}/average mole unit,* versus about 33 A.^{2}/average mole unit for the branched PVBz–stearic acid mixture. The linear PVBz–stearic acid mixture shows a lower surface pressure at large areas than the branched PVBz–stearic acid mixture. We reported previously the observation of an unusual contour of the isotherm for the mixture of branched PVBz–stearic acid at low pressure.[2,3] The isotherm rises abruptly at about 27 A.^{2}/average mole unit and then levels off to form a reproducible plateau at 2 dyne/cm. (Fig. 2). Similar behavior is observed with the linear PVBz–stearic acid mixture, although the rise in pressure is more gradual and the low pressure plateau is shifted toward a smaller area. The possible explanations for this phenomenon are rearrangement, repacking, or complex formation between the two components of the mixtures.[2,3] It is necessary to note that the linear PVBz–stearic acid mixture appears to undergo this phenomenon while being compressed to relatively smaller areas. However, pressure begins to rise abruptly at about 14 A.^{2}/average mole unit. With further decrease in area, the surface pressure rises to 36 dyne/cm., when collapse is observed. The behavior of the linear PVBz–stearic acid mixture is very similar in this respect to the corresponding mixture of the branched polymer. The displacement of the steep portion of the isotherm of the former by about 2 A.^{2}/average mole unit and the longer plateau at 2 dyne/cm. may be indicative of a better repacking or rearrangement of the two components of the mixture. The collapse pressure for the two films is practically identical (36 dyne/cm.) and is lower than the collapse pressure of the individual components when spread by themselves. The cross-sectional area at extrapolated zero pressure is 12.2 A.^{2}/average mole unit as compared to 14 A.^{2}/average mole unit for the branched PVBz–stearic acid mixture. Compressibility is 0.0036 cm./dyne, practically identical with that of the corresponding branched PVBz mixture.

* The average mole unit is calculated on the basis of the mole ratio of the two components in the equiweight binary mixture.

Hysteresis experiments with linear PVBz–stearic acid mixtures showed effects similar to those observed with the corresponding branched PVBz–stearic acid mixture, as described by us elsewhere.[3]

CONCLUSIONS

The similarity of the pressure–area isotherms, for the linear and branched PVBz and their mixtures with stearic acid is in agreement with the general mechanistic conclusions on vinyl benzoate polymerization.[10] The termination of the stabilized aromatic radical is predominantly with growing polymer vinyl radicals. The resulting macromolecule consists of a backbone chain interspersed with occasional long branches emanating off some phenyl groups. For packing and orientation toward a polar surface, these branches would behave similarly to the backbone chain. If termination by primary vinyl radicals was a predominant reaction, one would expect a different surface behavior. The short branches would then consist of disubstituted aromatic moieties. These could have a plasticizing action[3] and contribute to a net surface pressure–area isotherm for branched poly(vinyl benzoate) different from that for the linear material.

Support for these conclusions was derived by the examination of the nuclear magnetic resonance spectra of the two types of poly(vinyl benzoate). The spectra were taken at room temperature from a 5% solution of the polymers in C_6D_6, on a Varian A-60 high resolution NMR spectrometer (Fig. 3). If a significant portion of disubstituted aromatic groups was present (more than 3–4%), one would observe a splitting in the phenyl–hydrogen peaks, a chemical shift to higher field values, and a difference in the —CH and —CH₂ relative peak positions for the two polymers. None of these could be detected. The NMR spectra of the two polymers are almost superimposable. (The apparent splitting of the peak at ~7.18 ppm is due to the presence of C_6H_6 as impurity in the deuterobenzene solvent.)
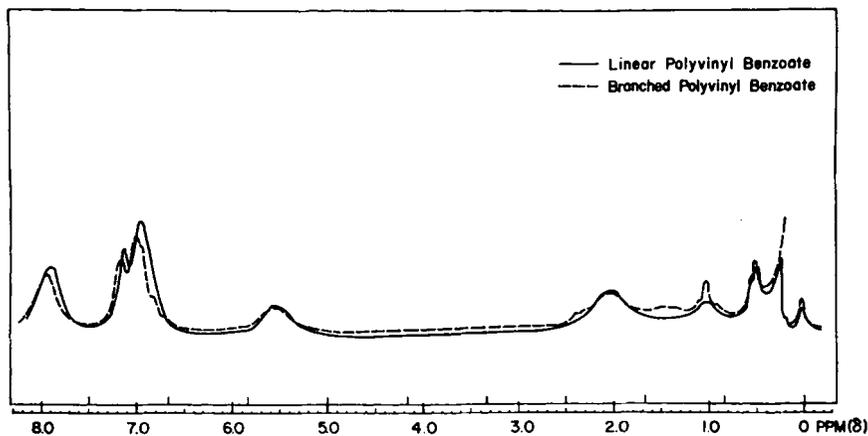

Fig. 3. NMR spectra for (———) linear and (- -) branched poly(vinyl benzoate).

The present study indicates that branching in poly(vinyl benzoate) is not the underlying cause for the unexpected monolayer film characteristics of these polymers. The alternative explanations[3] of increased cohesive forces between coplanar aromatic rings in contiguous parallel alignment, or the possibility of alternation in opposite directions, could account for tighter packing, a smaller area and a stronger film. Because of the increased thickness of the monolayer films from that calculated, one can not neglect the possibility of some rigid coils or folds raising from the surface on compression and packing tightly.

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Résumé

Les films monomoléculaires du benzoate de polyvinyle (PVBz) et de mélanges de PVBz linéaire avec l'acide stéarique ont des propriétés similaires à ceux du PVBz ramifié et de ses mélanges avec l'acide stéarique. Le spectre de résonance magnétique nucléaire du PVBz linéaire et ramifié ne montre aucune séparation phényle-hydrogène, ni de shift chimique ni d'autres différences dans les positions relatives des pics. Ces résultats sont en accord avec la structure de PVBz tel qu'on l'obtient à partir de considérations mécaniques générales. Les propriétés inhabituelles des films monomoléculaires obtenus

à partir de ce polymère, peuvent être attribués à l'alignement contigu des noyaux aromatiques et à un tassement plus serré mais non à la ramification.

Zusammenfassung

Monomolekulare Filme aus linearem Polyvinylbenzoat (PVBz) und aus Mischungen aus linearer PVBz-Stearinsäure zeigen ähnliche Eigenschaften wie verzweigtes PVBz und seine Mischungen mit Stearinsäure. Kernmagnetische Resonanz von linearem und verzweigtem PVBz zeigt keine Phenolwasserstoffaufspaltung, chemische Verschiebung oder andere Unterschiede in der relativen Lage der Maxima. Diese Ergebnisse bestätigen die aus allgemeinen mechanistischen Überlegungen (10) abgeleiteten Struktur von PVBz. Die ungewöhnlichen Eigenschaften der monomolekularen Schichten dieses Polymeren können der günstigen Anordnung der aromatischen Ringe und der dichteren Packung, nicht aber einer Verzweigung zugeschrieben werden.