

Effect of Chemical Structure on Physical Properties of Isomeric Polyesters

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The objective of this work has been to study the effect of changes in chemical structure of polyester intermediates on the physical properties of a carefully selected group of polyesters, all of which are produced by systematic variations in the arrangement of the component groups in a series of intermediates which will produce polymers having identical total chemical composition.

EXPERIMENTAL

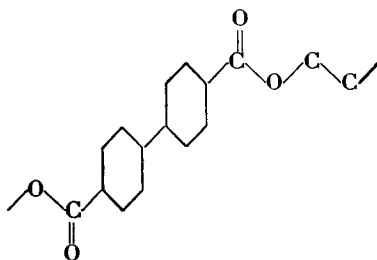
In this study polyethylene bibenzoate has been systematically substituted by two methylene radicals, in most of the possible configurations that do not result in producing unsymmetrical intermediates. Properties of the polymers vary from high melting very crystalline products such as polytetramethylene bibenzoate through amorphous, quite tough, fairly high softening polymer such as polyethylene 2,2'-dimethyl-4,4'-biphenyldicarboxylate to polyethylene 4,4'-biphenyldiacetate, a very low softening amorphous polymer.

All polymers discussed in this paper have been produced by ester alcoholysis using the indicated glycol and the methyl ester of the indicated dibasic acid. Litharge in most cases has been the catalyst and where possible polymerization has been carried out at 260° and 1 mm.

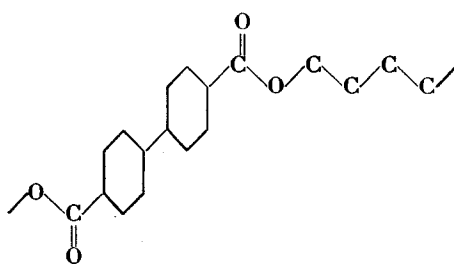
TABLE I

Acid X	M. p. DMX, °C.	M. p. or softening point, 2GX, °C. ^a	T _g , °C.
Bibenzoic acid	212	>300c	>100
4,4'-Biphenyldiacetic acid	71	150a	Low
<i>p,p'</i> -Ethylenedibenzoic acid	119	212c	—
<i>p,p'</i> -Ethylidenedibenzoic acid	Liq.	100a	Low
2,2'-Dimethyl-4,4'-biphenyldicarboxylic acid	100	>200a	73
		4GX	
Bibenzoic acid	212	280	>100

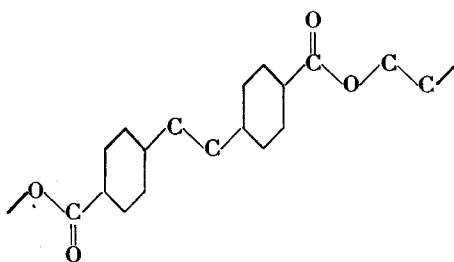
^ac, crystalline, a, amorphous. DMX, dimethyl ester. 2GX, ethylene polyester. 4GX, tetramethylene polyester. T_g, second order transition temperature of polymer.



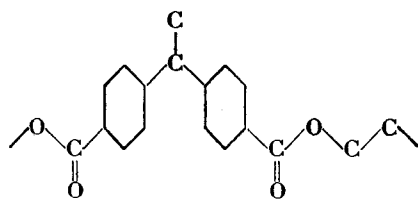
Formula 1



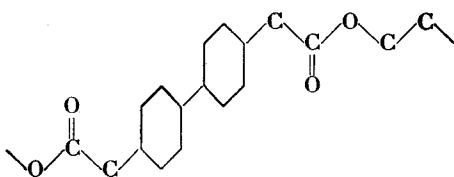
Formula 2



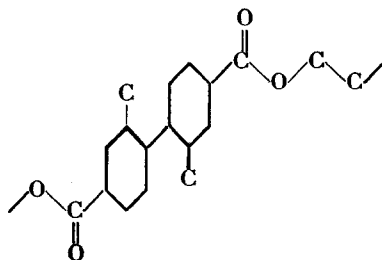
Formula 3



Formula 4



Formula 5



Formula 6

Polyethylene bibenzoate melts well above 300°C. and cannot be prepared by a normal fusion procedure. Higher derivatives, such as polyhexamethylene bibenzoate which melts at about 230°C., are so highly crystalline that they cannot be obtained in the amorphous form.

In order to study the effect of distribution of components with no change in molecular weight, the total over-all structure of the recurring unit, polyethylene bibenzoate, shown in Formula 1 has been altered by systematic substitution of two methylene groups into the structure at various places. The data on the physical properties of all the various polymers will be found in Table I.

By introducing two methylene radicals into the glycol chain polytetramethylene bibenzoate represented by Formula 2 is obtained. Polytetramethylene bibenzoate melts at about 280°C. and is believed to have a transition temperature above 100°C. though it cannot be measured on account of extreme crystallinity. This structural change has in no way affected the resonance of the bibenzoate radical. Both carboxyls are attached to the aromatic rings and the aromatic rings are attached to each other so that resonance possibilities are rather large.

Interposition of the two methylene radicals between the two benzene rings gives the ethylene polyester of *p,p'*-ethylenedibenzoic acid shown schematically in Formula 3. This substitution has separated the aromatic nuclei and there is a somewhat marked drop in melting point but this polymer is still highly crystalline. A preliminary indication of the effect of these substitutions can be gained by an inspection of the melting point of the dimethyl esters shown in the second column of the table.

When two methylene groups are substituted between the two aromatic nuclei to give an unsymmetrical 1,1-ethylidene group shown in Formula 4, the effect is much more pronounced. In this case the methyl ester is a viscous liquid, and the polymer is a low melting amorphous product which has not been crystallized. This effect is at least in part due to the odd number of atoms in the polymer chain but may be due partially to the fact that there is a side chain in this structure. Coffman, Berchet, Peterson, and Spanagel¹ have shown the effect of an odd number of atoms between polar groups on the melting points of numerous aliphatic polyamides and without exception an odd number of atoms markedly lowers the melting point. Also, Hill and Walker² have shown that methyl groups as a side chain have

a marked effect on the melting point and crystallinity of polyesters. For example, they give the following melting points:

Polyethylene terephthalate.....	256°C.
Polypropylene terephthalate.....	122°C. (amorphous sticking temp.)
Polytrimethylene terephthalate.....	221°C.

When the two methylene groups are separated and placed between the carboxyl groups and the benzene rings, polyethylene 4,4'-biphenyldiacetate indicated in Formula 5 is produced. Here the effect of the substitution is very marked. While the resonance of the two phenyl groups has not been destroyed, the effect produced by having a carboxyl attached directly to a benzene ring has been upset with the result that this polymer is very low melting and amorphous although there are some indications that it can be crystallized on annealing. The physical properties indicate that substitution of the methylene groups in this position has a much more pronounced effect than separating the two aromatic nuclei indicated in Formula 3. This appears to establish the necessity for having the carbonyl group in aromatic polyesters directly attached to the ring in order to achieve high melting point and high strength.

The above possibilities about exhaust places in which the two methylene groups can be placed directly in the chain without producing unsymmetrical substitution. However, it is possible to place the two radicals as side groups on the aromatic ring with interesting results. When they are placed in the 2,2'-positions on the two rings the polyethylene 2,2'-dimethyl-4,4'-diphenyldicarboxylate represented by Formula 6 is obtained. In this case the carboxyls are still attached to the rings and the rings are attached to each other but the presence of methyl groups in the 2,2'-positions make it impossible for the aromatic rings to lie in the same plane. O'Shaughnessy and Rodebush³ have shown that methyl groups substituted in these positions on the diphenyl structure bring about a marked reduction in ultraviolet absorption and they attributed this to the impossibility of the two rings becoming coplanar and therefore they have very little resonance. Whether the effect in this new polyester is due entirely to the inability of the structure to assume a coplanar configuration or is partly affected by the substituent methyl groups hindering close chain packing of the molecules in a crystal is not clear. Nevertheless, this substitution interferes with their crystallizability in a very marked manner and also interferes with resonance possibilities of the whole molecule. This substitution does not result in as marked lowering of the melting point of the methyl ester as was the case where the aromatic rings were removed from the carboxyls, nor does it result in such a marked lowering of the sticking point of the polymer. Nevertheless the polymer is entirely amorphous and has not been crystallized by normal means. Its sticking point (200°C.) is unusually high for an amorphous polymer; its transition temperature as determined by the standard dilatometric method is 73°C.

References

- (1) Coffman, D. D., Berchet, G. J., Peterson, W. R., and Spanagel, E. W., *J. Polymer Sci.*, **2**, 306 (1947).
- (2) Hill, R., and Walker, E. E., *J. Polymer Sci.*, **3**, 609 (1948).
- (3) O'Shaughnessy, M. T., and Rodebush, W. H., *J. Am. Chem. Soc.*, **62**, 2906-11 (1940).

Synopsis

It has been shown that changes in chemical structure of aromatic polyesters have a pronounced effect on the melting points and crystallinity of the polymers. Changes which remove the carboxyl group from the ring result in marked lowering of the melting point and toughness of the polymers. Changes which separate aromatic nuclei lower melting point but not as markedly as the above change. Changes which put an odd number of atoms in the polymer chain markedly lower the melting point. Changes which interfere with the possibility of co-planarity of the components very markedly affect the crystallinity, and to a lesser extent the sticking point of polymers.

Résumé

On a montré que des changements apportés dans la structure chimique des polyesters aromatiques exercent un effet marquant sur les points de fusion et la cristallinité des polymères. Les changements qui éloignent le groupe carboxylique du noyau entraînent une diminution marquée du point de fusion et de la dureté des polymères. Les modifications qui séparent les noyaux aromatiques abaissent le point de fusion de façon moins nette toutefois que les changements précédents. Les changements qui introduisent un nombre impair d'atomes dans les chaînés polymériques abaissent le point de fusion. Les modifications qui interfèrent avec les possibilités de coplanéité des composants influencent très nettement la cristallinité, de même que le point de solidification des polymères, bien qu'en proportion moins marquée.

Zusammenfassung

Es wurde gezeigt, dass Änderungen der chemischen Zusammensetzung aromatischer Polyester einen starken Einfluss auf Schmelzpunkt und Kristallinität der Polymeren haben. Veränderungen, die die Carboxylgruppe vom Ring entfernen, bewirken eine merkbare Erniedrigung von Schmelzpunkt und Zähigkeit des Polymers. Veränderungen, die aromatische Ringe abtrennen, erniedrigen den Schmelzpunkt, aber nicht so stark wie die oben erwähnten. Veränderungen, die eine ungerade Atomzahl in die Polymerkette einführen, erniedrigen den Schmelzpunkt merklich. Veränderungen, die mit der Möglichkeit für Coplanarität der Komponenten interferieren, beeinflussen stark die Kristallinität, aber weniger stark den Klebepunkt der Polymeren.

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