The Effect of Chemical Structure of Derivatives of 1,1-Bis(4-hydroxyphenyl)-2,2-propane on the Antiplasticization of Polycarbonate

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Synopsis

The antiplasticizing effect of ester derivatives of bisphenol A: 1,1-bis(4-hydroxyphenyl)-2,2-propane diacetate (DAPP), 1,1-bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane diacetate (DACPP), 1,1-bis(4-hydroxy-3,5-dibromophenyl)-2,2-propane diacetate (DABPP), 1,1-bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane dibenzoate (DBCPP), 1,1-bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane di-2,4-dichlorobenzoate (DCBCPP) on polycarbonate was investigated. Obtained results indicate that antiplasticizing abilities of these compounds depend on the number of polar groups in the molecule, as well as on the possibility of tight filling the free volume by the molecules in polymer–antiplasticizer system.

INTRODUCTION

The stiffening of polymer by the addition of low-molecular-weight compounds soluble in it is termed antiplasticization.[1-3] According to many investigators[1-7] this phenomenon is due to the molecular interactions. In our prior studies[4-6] Doolittle's theory[8-11] of plasticization was developed on the systems in which the additive molecule interacts simultaneously with two (or more) polymer macromolecules. It was also shown that plasticization and antiplasticization phenomena are closely related and the same low-molecular-weight substance can act as a plasticizer or antiplasticizer depending on the temperature and its content in the system. When the interactions of the additive molecule with two (or more) macromolecules are stronger than the interactions of the molecules themselves on the definite segment of the polymer chain, antiplasticization occurs.[4-6]
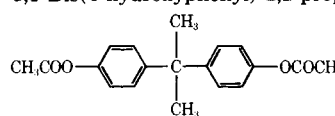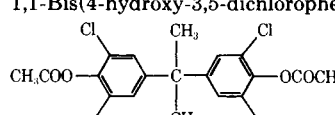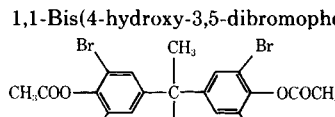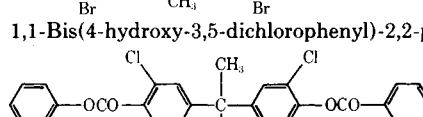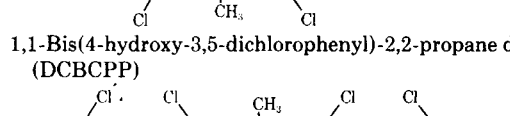
The magnitude of intermolecular interactions in polymer–antiplasticizer system depends on the chemical structure of the antiplasticizer molecule, its polarity, and dimension. The aim of this study is to discuss the above correlations.

EXPERIMENTAL

Materials

As antiplasticizers for polycarbonate (PC) we chose the ester derivatives of bisphenol A containing a varying number of polar groups and aromatic rings. They are given in Table I.

TABLE I

Additive	Melting Point (°C)
1,1-Bis(4-hydroxyphenyl)-2,2-propane diacetate (DAPP)	92–93

1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane diacetate (DACPP)	135–137

1,1-Bis(4-hydroxy-3,5-dibromophenyl)-2,2-propane diacetate (DABPP)	175–176

1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane dibenzoate (DBCPP)	202–203

1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane di-2,4-dichlorobenzoate (DCBCPP)	187–188

We compared the antiplasticizers used with 1,1-bis(4-hydroxy-3,5-dichloro-phenyl)-2,2-propane diacetate (DACPP) as its good antiplasticization properties are known.[5,12,13]

The synthesis of the above compounds was carried out as follows:

(1) 1,1-Bis(4-hydroxyphenyl)-2,2-propane diacetate (DAPP) was prepared by heating at reflux condenser for 2 hr bisphenol A (1,1-bis/p-hydroxyphenyl/-2,2-propane) (1 mol) and acetic anhydride (4 mol) in the ratio 1:4. The resultant mixture was cooled, the product was precipitated and recovered as a filter cake, which was washed with water. The product was dried in the air and it had melting point of 92–93°C.

(2) 1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane (CPP) was conducted in the manner described in Ref. 14. Into a three-necked round-bottomed flask, equipped with stirrer, dropping funnel, and reflux condenser connected with the absorber of hydrogen chloride, 57 g of bisphenol A and 274 ml of acetic acid were placed. The reaction mixture was stirred and heated at 50°C. Then 85 ml of sulfuryl chloride was added in such a way that the temperature of the re-action mixture never exceeded 60°C. During this process the intense evolution of hydrogen chloride was observed. Then the reaction mixture was heated at 115°C for 1 hr. The contents of the flask was then cooled and the product was precipitated. The product was separated by filtration, washed with small amount of acetic acid, and dried in the air. Melting point of the product is 135–136°C, yield 65–70 g.

(3) 1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane diacetate (DACPP) was prepared according to Łukasik.[14] In a round-bottomed flask equipped with reflux condenser 70 g of CPP and 100 ml of acetic anhydride was heated at reflux for 2 hr. The resultant mixture was cooled and the crystalline product was precipitated. DACPP was isolated by a filtration operation, washed with acetic acid, dried in the air, and recrystallized from the mixture of acetic anhydride and acetic acid (volumetric ratio 3:1). The obtained product has melting point of 135–137°C, yield 55 g.

(4) 1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane dibenzoate (DBCPP) was obtained in the following manner: stoichiometric amounts of CPP and benzoyl chloride were heated at 140°C for 2 hr under the reflux condenser. The intense evolution of hydrogen chloride was observed. Then the contents of the flask were dissolved in the smallest amount of benzene. The product was precipitated by dropping methanol into the above solution and cooling the mixture. The crystalline product was separated by filtration and dried in the air. Melting point of the product is 202–203°C, yield 70%.

(5) 1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane di-2,4-dichlorobenzoate (DCBCPP) was prepared in the same manner as DBCPP using 2,4-dichlorobenzoyl chloride instead of benzoyl chloride. DCBCPP melts at 187–188°C.

(6) 1,1-Bis(4-hydroxy-3,5-dibromophenyl)-2,2-propane (DBP) was prepared according to the following schedule: Into the round-bottomed flask equipped with a stirrer, reflux condenser, and droplet funnel, 25 g of bisphenol A, 36 ml of methanol, and 15.5 ml of water were placed. The mixture was intensively stirred until bisphenol A was dissolved. Then 65.2 g of bromine was added with such a speed that the temperature did not exceed 35°C. The white product precipitated and hydrogen bromide intensively evoluted. The contents of the flask were allowed to stand overnight. Then the mixture was heated at reflux for 15 min, cooled, the crystalline precipitate was isolated by filtration and dried in the air. Yield is 52 g of DBP, which has a melting point of 175–176°C.

(7) 1,1-Bis(4-hydroxy-3,5-dibromophenyl)-2,2-propane diacetate (DABPP). In a round-bottomed flask, 52 g of DBP and 50 ml of acetic anhydride were heated at reflux for 2 hr. The product was precipitated after cooling and it was dried in the air. DABPP was recrystallized from 30 ml of acetic acid. It has a melting point of 169–170°C, yield 55 g.

Sample Preparation

Commercial bisphenol A polycarbonate Makrolon 3200, a product of Bayer (Germany), having a viscosity-average molecular weight $\overline{M}\eta \simeq 30{,}000$[15] was used in the investigations. The films were prepared by pouring 5% solutions of the polymer and the antiplasticizer being tested in methylene chloride in the manner described previously.[5,6,16]

Measurements

Tensile stress–strain measurements were made at 20°C and 60% relative humidity on the 60–70 μm films with an Instron TMM testing machine. A draw rate was 0.05 m/min. From the plots it was easy to obtain the tensile strength

and elongation at break as well as the tensile modulus, which was calculated from the initial linear slope of the stress–strain curves.

Molar volumes V_{mol} of the polycarbonate films containing the additives were calculated from the following relation

$$V_{mol} = \frac{M_{av}}{d^t}$$

where d^t is the density of the film sample measured at 25°C in a gradient column filled with an aqueous NaI solution and water in the ratio 4:1,[17] M_{av} is the mass of average mole of the solid solution derived from the equation:

$$M_{av} = \sum_{i=1}^{n} n_i M_i$$

where n_i represents mole fractions of the components of the solution, i.e., low-molecular-weight additive and polycarbonate, and M_i is their molecular weights.

The theoretical molar volume $V_{mol,t}$ for each sample was calculated also using the relationship of volume additivity:

$$V_{mol,t} = n_1 V_{mol\ 1} + n_2 V_{mol\ 2}$$

in which V_{mol1} and V_{mol2} are the molar volumes of the polymer and the antiplasticizer, respectively, and n_1, n_2 are their molar fractions.

RESULTS AND DISCUSSION

There have been no methods until now which can precisely determine the magnitude of intermolecular interactions in the antiplasticized polymers. However, it is likely that the tensile strength of the polycarbonate film and its Young's modulus depend on the molecular interactions. That is why the studies of mechanical properties of polymeric films can give us the indirect evidence about the Van der Waals interactions between the macromolecules of polycarbonate and the low-molecular-weight additives.

In concentration-dependence studies of the properties of polycarbonate–additive systems we did not express the concentration in weight percentage as before[1–6] because it is difficult to compare the efficiency of different antiplasticizers owing to their various densities. That is the reason for the use of molar concentrations in data elaboration. They were calculated taking into account the difference in the length of antiplasticizer molecules. That is to say, one aromatic ring in a low-molecular-weight compound corresponds to one aromatic ring in a polycarbonate macromolecule. It means that one molecule of the acetate derivative of bisphenol A corresponds in our calculations to one polymer mer, while one molecule of benzoate derivative to two polymer mers.

The correlations of tensile strength and tensile modulus of polycarbonate (PC) films containing varying amounts of low-molecular-weight substances are plotted in Figures 1 and 2. It can be easily seen that (1) all substances under investigation are very effective as antiplasticizers, including DAPP which does not contain the chlorine atoms in its structure; (2) the bigger the antiplasticizer molecule is, the lower is the molar concentration at which the mechanical properties of antiplasticized polymer reach the maximum values; (3) the increase
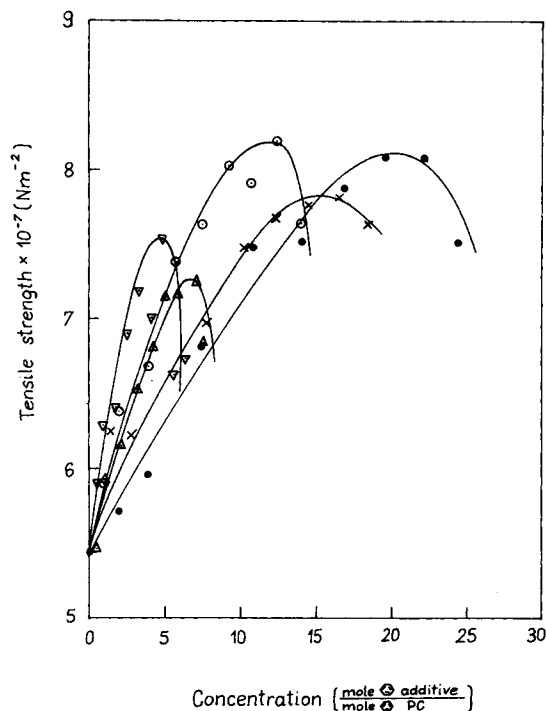
Fig. 1. Tensile strength σ of the antiplasticized PC films vs the molar concentration of ●, DAPP; ×, DACPP; ⊙, DABPP; ▲, DBCPP; ▽, DCBCPP.

from two to four in the number of aromatic rings in the antiplasticizer molecule does not improve its efficiency.

Apparently surprising is the fact that DAPP, having a structure similar to that of the PC mer and not containing the additional polar atoms, is quite effective as PC antiplasticizer. The magnitude of intermolecular interactions depends on the type and number of polar groups in the molecules, as well as the distances between them. It is obvious that the Van der Waals interactions are inversely proportional to the distance between the molecules to the power of six. Therefore, even slight approach of one molecule to another can increase the energy of their interactions.

We obtained the value ΔV, i.e. the difference between the molar volume of the sample achieved from the experimentally measured density of the film in a gradient column and those calculated additively taking into account the molar volumes of the components of the polymer composite.

The correlations between ΔV and the molar concentrations of the additives are plotted in Figure 3. For DAPP the molar volumes difference has a negative value. It means that the molecules are closer together and the intermolecular interactions are stronger. As a result the increase in tensile modulus and the tensile strength is observed.

In the case of the polymeric films containing DACPP and DABPP an increase in the molar volume difference ΔV is seen in the certain range of the additive content. It may be due to the fact that it is much more difficult to pack tightly the antiplasticizer molecules containing two chlorine or bromine atoms between the macromolecules of polycarbonate than DAPP molecules. However, in the
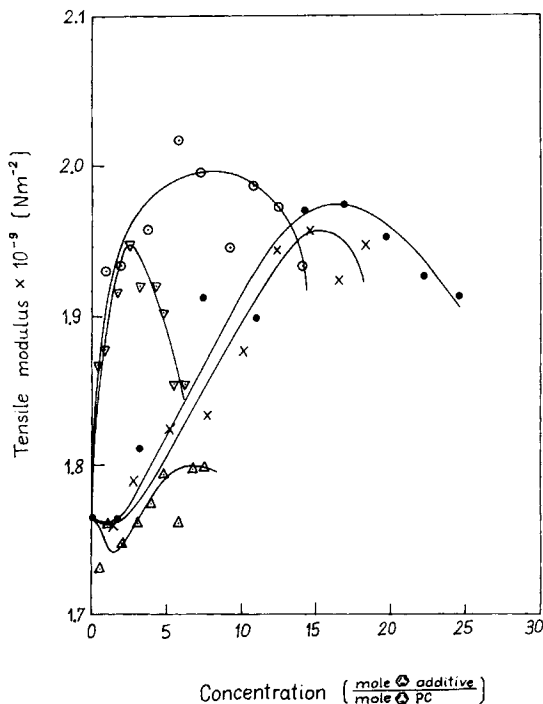
Fig. 2. Dependence of the tensile modulus E on the additive content for PC films antiplasticized with ●, DAPP; ×, DACPP; ☉, DABPP; △, DBCPP; ▽, DCBCPP.

above cases the polarity growth of DACPP and DABPP molecules has greater influence than increase of the intermolecular distances and the antiplasticization occurs (Figs. 1 and 2). ΔV for these film samples has a negative value when the additive content is high. But the PC films containing more than 12 or 15 mol% of DABPP or DACPP are very stiff and brittle and that is why their tensile strength decreases. In the case of the PC film containing the four-ring additives as DBCPP and DCBCPP two factors should be taken into account: increasing polarity and decreasing distances between the interacting molecules.

For these two substances ΔV has a negative value (Fig. 3) therefore the decrease in the intermolecular distances occurs. But DCBCPP molecule is much more polar (it contains eight chlorine atoms per molecule) than DBCPP molecule which has only four chlorine atoms in its structure. It can be seen from the Figures 1 and 2 that the increase of the polarity of the additive molecule results in a higher antiplasticizing effect.

It is interesting to observe that the bigger the antiplasticizer molecule is, the lower is the molar concentration at which it reaches its greatest efficiency (Figs. 1 and 2). It could be interpreted as a result of the tighter packing of the small antiplasticizer molecules in the matrix of PC than of the bigger ones.

Thus the increase of the intermolecular interactions may be regarded as a resultant of two parameters: the changes in the polarity of the antiplasticizer molecules and the changes in intermolecular distances. But the influence of these two components is for the moment very difficult to estimate taking into consideration the present state of the measuring technique.

Our studies showed that the increase of the number of aromatic rings in the
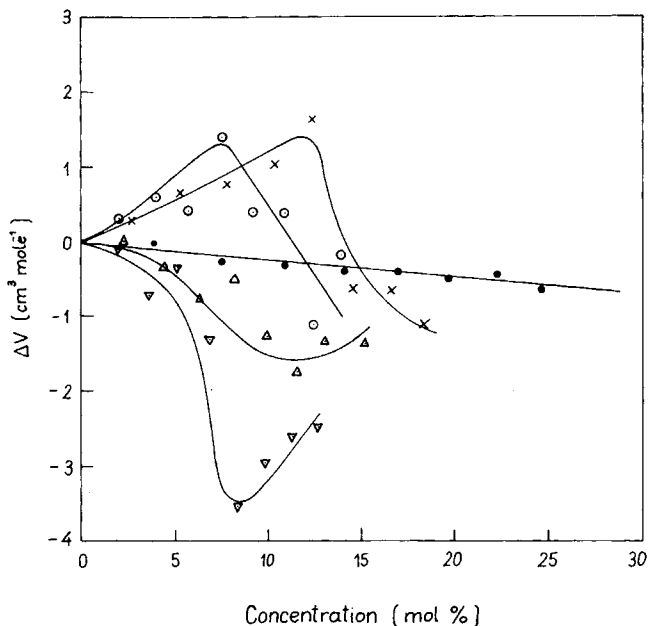
Fig. 3. Relationship between ΔV (for explanation see the text) and molar concentration of the following antiplasticizers ●, DAPP; ×, DACPP; ⊙, DABPP; ▲, DBCPP; ▽, DCBCPP.

additive molecule (from two to four) did not improve the antiplasticization properties of DBCPP and DCBCPP compared with DACPP. As related by Jackson and Caldwell[2] the antiplasticizer molecule should possess at least two nonbridged aromatic rings. Our studies did not prove it. On the contrary DBCPP and DCBCPP appeared to be less effective antiplasticizers than DACPP. Symmetric trinitrotoluene [TNT][6] which has only one aromatic ring was an active antiplasticizer for PC, as well as tetracyanoethylene [TCNE][18] which has no aromatic ring at all. TCNE, which forms with PC a charge transfer complex having, in UV spectra, an absorption band near 330 nm, increases the tensile strength from 5.5×10^7 N/m² [pure PC foil] to 6.2×10^7 N/m² [PC foil containing 6 wt% of TCNE] as well as tensile modulus from 1.7×10^9 N/m² to 2.1×10^9 N/m², respectively. It was difficult to prepare the PC foils containing higher concentration of TCNE since it crystallizes separately during the evaporation of the solvent.[18] On the other hand, TNT being more soluble in PC exhibits antiplasticating properties in a wider range of concentrations.[6]

In numerous papers[19,20] the antiplasticization properties of low-molecular-weight compounds are connected with the mobility of their molecules. In that case the doubling of the aromatic rings in the additive molecule should decrease its mobility and, consequently, increase its antiplasticizing ability. But our experimental data did not prove it.

In relation with our research work we can say that the main reason for antiplasticization phenomenon is considered to be the increase of intermolecular interactions in the polymer–antiplasticizer system. Their magnitude depends on the polarity and the distances between the interacting molecules.

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