

Refractometric and Calorimetric Studies of the Van der Waals Interactions Between the Molecules of Polycarbonate and of the Additives Acting as Plasticizers or Antiplasticizers

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Synopsis

Considerable deviations of molar refraction from the additivity in the solutions containing polycarbonate and its antiplasticizers symmetrical trinitrotoluene and 1,1-bis(4-hydroxy-3,5-dichlorophenyl)2,2,2-trichloroethane diacetate are reported. In contrast to this, the solutions of polycarbonate with plasticizer di-*n*-butyl phthalate and the solutions of antiplasticizers in pure solvent show only insignificant deviation from the additivity. The calorimetric studies showed the differences in the heats of solution of the used antiplasticizers in pure solvent and in the solvent containing a constant amount of polymer, whereas there was no noticeable difference in the polycarbonate-plasticizer (di-*n*-butyl phthalate) system. Both deviations of the molar refraction from the additivity and differences of the heats of solution prove the existence of strong interactions between the molecules of polycarbonate and the antiplasticizer.

INTRODUCTION

It is well known that the addition of a low molecular weight substance soluble in the material results in decreasing the tensile modulus and the tensile strength. This phenomenon, termed plasticization, was explained as an effect of partial replacing of the interactions between the macromolecules by interactions of macromolecule-plasticizer molecule type.¹⁻⁴

The increase in tensile modulus and tensile strength was also observed in some low molecular weight substance-polymer systems in a definite range of concentrations and temperatures. This phenomenon, called antiplasticization,⁵⁻⁷ was not sufficiently interpreted though quite a number of studies have been made by several workers^{8,9} up to now.

One of the authors of this paper^{10,11} proposed the following conditions in which antiplasticization may occur: (1) the plasticizer molecule should interact simultaneously with two or more macromolecules; (2) these interactions should be stronger than the interactions of the molecules themselves on the definite segment of the polymer chain. If these conditions are fulfilled, physical crosslinking may occur increasing the tensile strength and the tensile modulus.

Thermal fluctuations make the intermolecular crosslinks unstable and effect dissociation. The equilibria of formation and dissociation of intermolecular crosslinks were examined in the paper,^{10,11} according to Doolittle's theory of plasticization.¹⁻⁴

Leuchs in his study discussed the possibility of the interactions of one plasticizer molecule with two macromolecules.¹² This concept seems to be reasonable, for only in the molecules of some plasticizers is the polar group shielded by hydrogen radicals and makes impossible the interaction with more than one macromolecule.

It is the purpose of this study to explain the mechanism of antiplasticization while paying special attention to the existence of strong interactions between low molecular weight compounds and macromolecules.

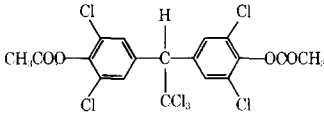
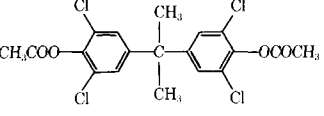
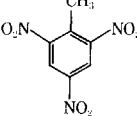
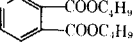
The paper discusses the experimental results on molar refraction, for even a small deviation from additivity can prove the existence of strong interactions between the compounds used.¹³ In addition, calorimetric studies were carried out to determine the effect of intermolecular interactions on the magnitude of the heat of solution in the polymer-plasticizer and polymer-antiplasticizer systems.

EXPERIMENTAL

Materials

Commercial polycarbonate Lexan, a product of General Electric Co. (U.S.A.) having an viscosity-average molecular weight $\bar{M}_\eta = 33,000$ was used in the investigations.

TABLE I
Compounds Used as Additives

Additive	Melting point, °C
1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2,2-trichloroethane diacetate (DCPE) ¹⁴	135-137
	
1,1-Bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane diacetate (DCPP)	91-92
	
Symmetrical trinitrotoluene (TNT) ¹⁴	81-82
	
Di-n-butyl phthalate (DBF) ¹⁵	
	

The compounds used as additives were substances giving an increase in tensile strength and the tensile modulus of polycarbonate in a wide range of concentrations.^{11,14} They are given in Table I.

Measurements of Molar Refraction

With regard to the difficulties in precise determination of the molar refraction of polycarbonate films containing varying concentration of plasticizer or antiplasticizer, we chose the indirect method. That is to say, we determined the molar refraction of DCPE, TNT, DBF after dissolving them in chloroform containing a definite amount of the polymer. The polymer (polycarbonate) content was constant (0.3814 g or 0.0015 mole per 100 ml), but the concentration of plasticizer or antiplasticizer varied from 0 to 120 wt-% at 10 wt-% increments with respect to the mass of the polycarbonate.

For control purposes, we determined the molar refraction of the solution of the low molecular weight compounds in pure solvent. It is evident that the concentration of the additives was the same as before, i.e., from 0 to 0.4577 g per 100 ml.

The measurements of the refractive indices were carried out on Pulfrich's refractometer (Carl Zeiss—Jena) at temperatures of $25^{\circ} \pm 0.05^{\circ}\text{C}$. The density was examined by the picnometer method at the same temperature.

The molar refraction was calculated from the well-known Lorentz-Lorentz equation:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M_{\text{av}}}{d} \quad (1)$$

wherein R is the molar refraction, in ml/mole; n is the refractive index of the solution used, d is the density of the solution used, in g/ml; M_{av} is the mass of average mole of the solution derived from the equation

$$M_{\text{av}} = \sum_{i=1}^n x_i M_i \quad (2)$$

where x_i represents mole fractions of the components of the solution, i.e., low molecular weight compound and chloroform (solvent) or low molecular weight additive chloroform and polycarbonate; and M_i represents molecular weights of the components of the solution.

Calorimetric Measurements

Since the additives are solid compounds at room temperature and insoluble in the solid polymer, it is very difficult to make direct measurements of the heats of solution of antiplasticizer and plasticizer in polycarbonate at the temperature in which the antiplasticization occurs.

So we did it in another manner and compared the heats of solution of the plasticizer and antiplasticizer in the pure solvent—methylene chloride and solution of polycarbonate in methylene chloride.

The plasticizers and antiplasticizers were the following compounds: DBP, DCPE, TNT, and DCPD, which was found as antiplasticizer, too.¹⁶

The concentrations of the low molecular weight compounds were 0 to 44

wt-% and 20 to 70 wt-% for DCPE, DBP, and TNT, DCPP, respectively. The mass of polycarbonate was constant (0.02 mole per 200 ml solvent).

Measurements were carried out at room temperature by means of the differential adiabatic calorimeter consisting of two 250-ml Dewar vessels, tightly closed with cork stoppers and put into a thermostat. Dewar vessels were the reference system and the proper measurement system. They were both equipped with a stirrer, glass tube (ampoule) with the substances to be investigated, two thermocouples of Constantan-copper, and additionally in the measurement system an electric heater for determining the heat capacity of the calorimeter.

The measurements were carried out as follows: 200 ml dry and distilled methylene chloride and an ampoule with the accurate amount of the low molecular weight compound were placed in each Dewar vessel. When tightly closed, the stirrers began to turn with steady but not very high speed. When the temperatures became equal in both vessels (it was evident from the straight line written by means of a pen on the paper on the temperature recorder connected with the thermocouples of the two Dewar vessels), the ampoule was broken. Then after several minutes, which were sufficient for the temperature to be equal again, the heat capacity of the calorimeter was determined.

The recorder used (Czechoslovak made) carried out the measurements with an accuracy of $\pm 0.001^\circ\text{C}$. The determination of the heat of solution was examined with the procedure usually applied in calorimetry.¹³

RESULTS AND DISCUSSION

The correlations of refractive index, density, and molar refraction calculated from them for the solutions of DCPE, TNT, and DBP in pure chloroform are plotted in Figures 1–3. As shown in Figures 1 and 2, the refractive index

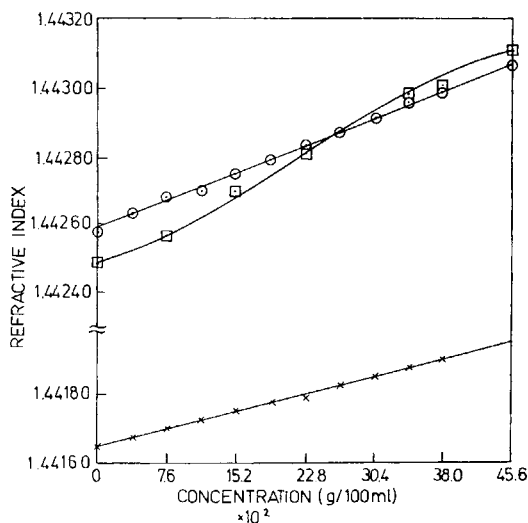


Fig. 1. Refractive index vs. additive content for the solutions of (□) TNT, (○) DCPE, (×) DBP in pure chloroform.

and density versus weight fraction of the soluble substance give straight or almost straight lines. The molar refraction calculated according to eq. (1) shows no deviation from the additivity, too.

In contrast to the above case, the polycarbonate solutions in CHCl_3 give

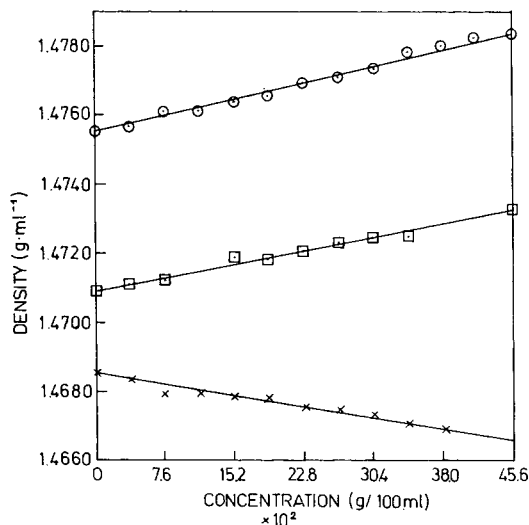


Fig. 2. Dependence of density on concentration of the solutions of (□) TT, (○) DCPE, (×) DBP in pure chloroform.

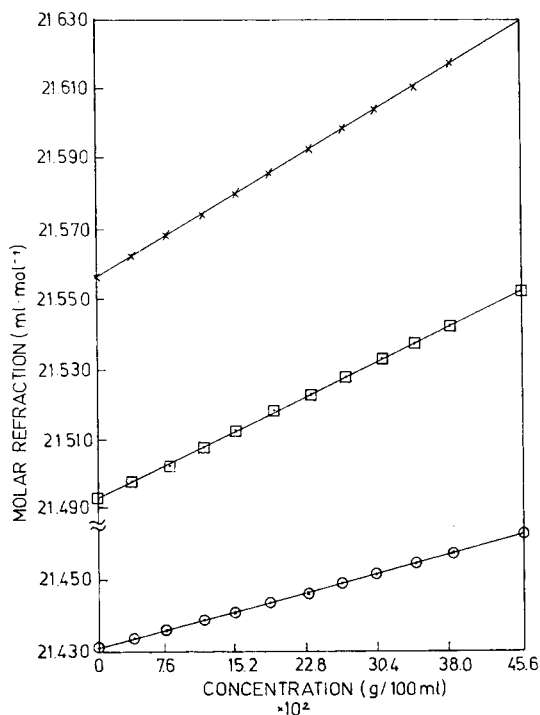


Fig. 3. Molar refraction-concentration relationship for the solutions of (□) TNT, (○) DCPE, (×) DBP in pure chloroform.

the other shape of the curves. As shown in Figure 4, there is no significant deviation of the molar refraction from the additivity when DBP is dissolved in a solution of polycarbonate in chloroform, and the curve has a convex shape. In the case of DCPE and TNT, the curves are different. The existence of minima of the molar refraction can be interpreted as a result of the strong interactions between the low molecular weight substance and the macromolecules of the polycarbonate.

In Figures 5–8, the values of the heat of solution are plotted as a function of

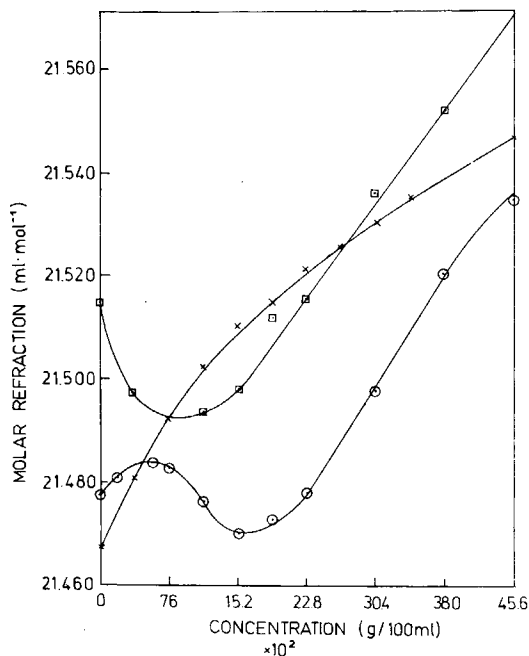


Fig. 4. Relationship between the molar refraction and the additive concentration for solutions of (□) TNT, (O) DCPE, (X) DBP in chloroform containing a given amount of polycarbonate.

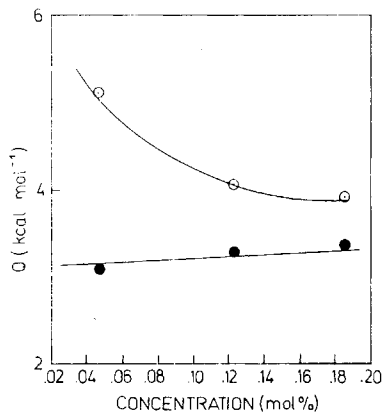


Fig. 5. Comparison of concentration dependence of the heats of solution of DCPE in pure methylene chloride (●) and in methylene chloride containing a given amount of polycarbonate (○).

the low molecular weight compound contents. As is shown, the heats of solution of the antiplasticizers TNT, DCPE, and DCPD in pure solvent and in the solution of polycarbonate in methylene chloride differ very much, whereas for

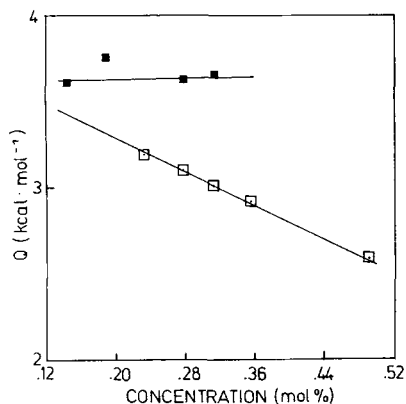


Fig. 6. Comparison of concentration dependence of the heats of solution of TNT (■) in pure methylene chloride and in methylene chloride containing a constant amount of polycarbonate (□).

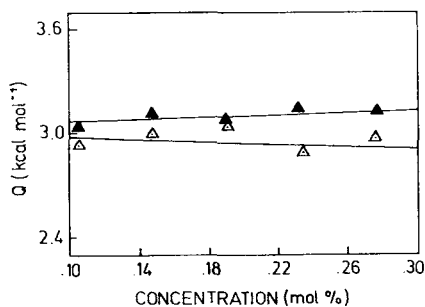


Fig. 7. Comparison of concentration dependence of the heats of solution of DCPD in pure methylene chloride (▲) and in methylene chloride containing a constant amount of polycarbonate (△).

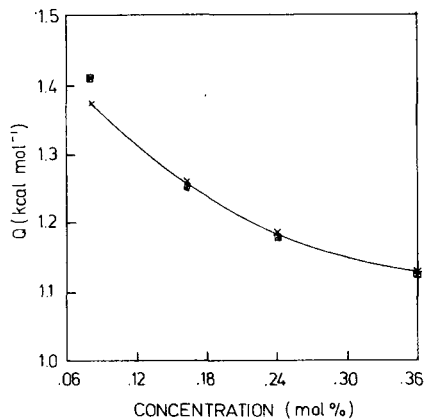


Fig. 8. Comparison of concentration dependence of the heats of solution of DBP in pure methylene chloride (×) and in methylene chloride containing a given amount of polycarbonate (*).

the plasticizer DBP the difference is within the limits of error (Fig. 8).

The above-mentioned behavior of DBP and the other low molecular additives may be explained as a result of strong interactions between the molecules of antiplasticizer and the macromolecules of polycarbonate, even when they are present in the solution. From this point of view, the interactions between the plasticizer and the polymer should be, if they really exist, much weaker.

The studies of the electric properties of the solution of polycarbonate and low molecular weight additives reported in reference 17 agree very well with the results related in the present study.

We must stress, however, that our measurements were carried out in solution, and that a good assumption can be made regarding strong interactions between the molecules of DCPE, DCPD, and TNT with the macromolecules of the polycarbonate in the system free of any solvent. These strong intermolecular interactions are the most probable reasons for different mechanical properties and the increase in stiffness (antiplasticization) of polycarbonate reported in a few studies.^{11,14,16}

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