Effect of High Pressure on Some Electrophysical Properties of Polymers: Polyconjugated Systems Doped by Iodine

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Synopsis

The effect of pressure P up to 2.5×10^3 MPa on the dielectric constant ϵ and conductivity G of a number of conjugated polymers doped by iodine has been studied. Polyphenylacetylene prepared with FeAcAc, polyphenylacetylene obtained with Ziegler catalyst, anionic polydiphenylacetylene, and polydiphenylbutadiene were chosen for investigation. It has been found that after doping the values ϵ and G increase and strongly depend on P. The possible mechanism of this phenomenon has been discussed.

INTRODUCTION

Doping of polyconjugated systems by electron acceptors, in particular, iodine, is known to increase essentially their specific electrical conductivity up to 10^5 $\Omega^{-1} \cdot m^{-1}$ for some doped polymers.[1,2] On the other hand, it has been recently found that the conductivity of low-molecular organic compounds with a developed conjugation system becomes higher under external pressure or under joint action of high pressure (HP) and shear deformation.[3-5] Thus, for example, under these conditions the transition of tetraphenylporphyrin into metal state has been observed, its electrical conductivity increasing at least by 6–7 orders of magnitude.[3]

In the present work we report the effect of pressure up to 2.5×10^3 MPa on the dielectric constant and conductivity of some conjugated polymers doped by iodine.

EXPERIMENTAL

Polyphenylacetylene prepared with FeAcAc (PPhA), polyphenylacetylene obtained with Ziegler catalyst (PPhAZ), anionic polydiphenylacetylene (PDPhA), and polydiphenylbutadiene (PDPhB) were chosen for investigation.

Iodine was introduced into the studied samples in amounts of 5–30 wt % both from gas phase and by mechanical mixing. The concentration of iodine in polymer was defined by weighting. The size of iodine particles used during mechanical mixing was 1–10 μm.

Gas phase doping of samples was carried out by two methods. The first one consisted of preparing a layer specimen by iodine deposition on the contact
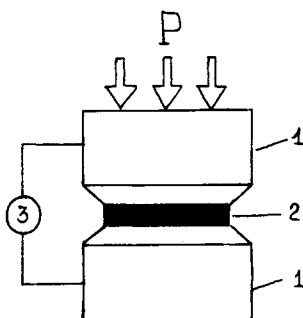
CCC 0021-8995/83/082467-06$01.60

Fig. 1. Block diagram of the apparatus used to measure electrophysical properties of conjugated polymers during their uniaxial compression: (1) Bridgman anvil; (2) sample; (3) measuring instrument. The arrows show the direction of compression.

surfaces of two cylindrical tablets obtained by polymer pressing at the pressure 2×10^2 MPa. In the second method the surface of a polymer powder was coated by iodine.

The experiments were carried out at room temperature according to the procedure described earlier.[6] The high pressure apparatus used was of Bridgman anvil type. Figure 1 illustrates the experimental configuration and the procedure for measuring the electrophysical properties of investigated substances during the uniaxial compression. An ac bridge operated at 1547 Hz was used as a measuring instrument to find the conductance G and the capacitance C of samples.

Both doped and undoped samples were obtained as cylindrical tablets by preliminary pressing at 200 MPa. In the pressure range $P \leq 4 \times 10^3$ MPa, the ratio of the thickness to the area of tablets has a constant value 6×10^{-1} m^{-1} with the accuracy 20% as follows from the available experimental data on the compressibility of organic solids.[7] Therefore, this quantity can be considered as a factor for a conversion of the data given as extrinsic values (e.g., conductance in Ω^{-1}) to those for intrinsic ones (e.g., conductivity in $\Omega^{-1} \cdot$m^{-1}).

RESULTS AND DISCUSSION

Typical dependences of the capacitance C on pressure P for "pure" PPhAZ and PPhA and for the same polymers doped by 5 wt % of iodine are shown in Figure 2. For comparison the similar dependence found for iodine is given in the same figure.

The analysis of C values, measured at constant pressure before and after doping, shows that the latter essentially increases the sample capacitance. Thus, after treating PPhA and PPhAZ by iodine at $P = 1.5 \times 10^3$ MPa, the capacitance increases by factors of 2.3 and 3.0, correspondingly. The dependence of C on P also changes after doping. For samples free of iodine the capacitance increases 1.5–2 as much as in the 10^2–10^3 MPa range of pressures, and, as the compression grows, it remains practically constant. The introduction of iodine leads to the disappearance of the saturation section on curves corresponding to the mentioned dependence, the values of C increasing 10 times for PPhAZ and 260 times for PPhA with P changing from 10^2 to 1.5×10^3 MPa. Similar changes of capacitance were observed under the effect of HP on PDPhA and PDPhB.
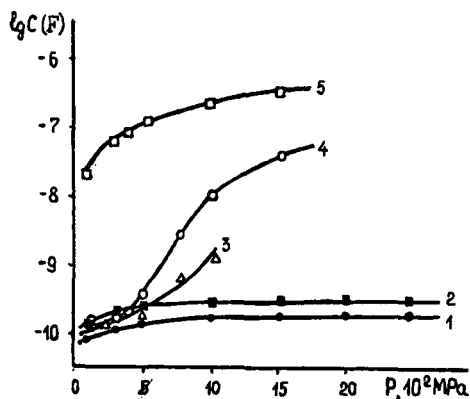
Fig. 2. Capacitance C of conjugated polymers and iodine vs. pressure P. The concentration of iodine in polymer matrix is equal to 5 wt %: (1) PPhA; (2) PPhAZ; (3) iodine; (4) PPhA doped by iodine; (5) PPhAZ doped by iodine.

After the pressure drop, the capacitance of samples decreased up to the value found under usual conditions for preliminarly pressed samples. The results, obtained in the first and all subsequent "compression–pressure drop" cycles, which were carried out after polymer doping at 3-min intervals for 1.5 h, agreed with each other with 10% accuracy. The reversible character of the effect shows that it is not connected with the extrusion of the substance from an interelectrode gap under HP. Also, it cannot be explained by a change in the sample thickness since the decrease in the volume of the investigated systems at $P \leq 4 \times 10^3$ MPa does not exceed 15–20%.[7] Thus we conclude that the capacitance increase observed is almost completely due to the increase of a dielectric constant ϵ under compression.
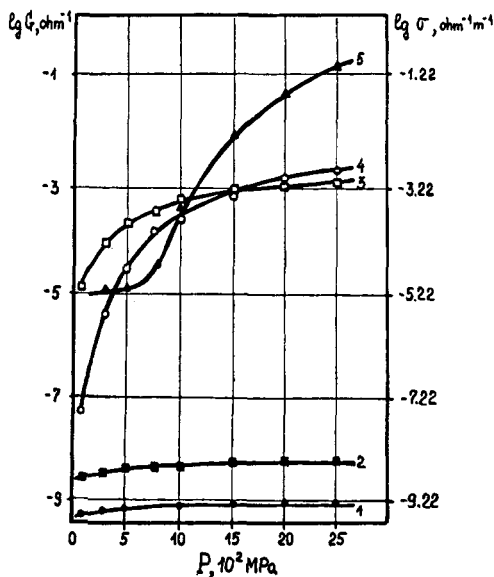

Fig. 3. Dependence of conductance G and conductivity σ on pressure P. The concentration of iodine in polymer matrix is equal to 5 wt %: (1) PPhA; (2) PPhAZ; (3) PPhAZ doped by iodine; (4) PPhA doped by iodine; (5) iodine.
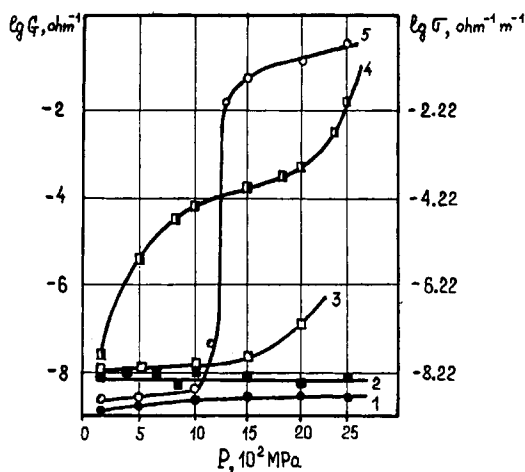
Fig. 4. Dependence of conductance G and conductivity σ on pressure P for PDPhB and PDPhA. The concentration of iodine in polymer matrix is equal to 5 wt %: (1) PDPhA; (2) PDPhB; (3) PDPhB doped by iodine after relaxation for 16 h in unloaded state; (4) PDPhB doped by iodine; (5) PDPhA doped by iodine.

The effect of HP on doped polyconjugated systems results not only in the change of their capacitance characteristics, but also in their ability to conduct the electric current. Corresponding dependences of the conductance G on P for the investigated polymers and iodine are given in Figures 3 and 4. Data presented in these figures for doped systems correspond to the iodine concentration of 5 wt %. The pressure dependences of the conductivity are also plotted in the same figures using the conversion factor mentioned in the previous section of the paper.

It can be seen that the absolute values of G and σ increases after doping. Moreover, after iodine introduction into polymer matrix, the effect of HP on the conductivity becomes more pronounced, G (and hence σ) rising with P for all the polymers studied. These changes as well as changes in capacitance, mentioned above, are reversible, i.e., after the removal of load the conductivity decreases up to the values obtained at atmospheric pressure for preliminary pressed samples. It should be noted that in the case when doped samples, subjected to high pressure for 1.5 h, were left for 16 h at the unloaded state, the effect of pressure on their conductivity as well as on the dielectric constant was observed at P to be essentially higher than at those required for the changing of electrical properties of similar unrelaxed samples (see Fig. 5, curves 3 and 2). This appears to be connected to the essential decrease in the concentration of iodine in the system as the result of its high volatility.

For doped polymers the abrupt increase of σ was observed at pressures close to those causing iodine transition into the high-conductive state.[8,9] In this connection it is interesting that at $P = 2.3 \times 10^3$ MPa the conductivity of some doped polyconjugated systems can reach or even exceed that of a doping agent under the same pressure. For example, such a situation takes place in the case of PDPhB and PDPhA.

Finally it should be noted that neither the dielectric constant nor the conductivity of the investigated doped polymers changed with the variation of the
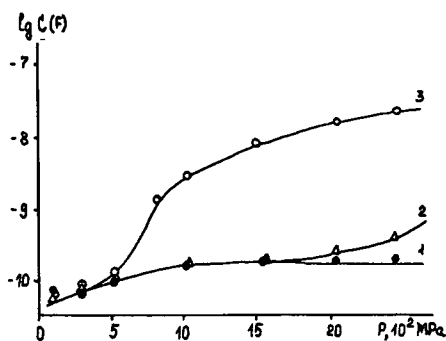
Fig. 5. The change of the dependence of capacitance C on pressure P with time for PDPhB. The concentration of iodine in polymer matrix is equal to 5 wt %: (1) PDPhB; (2) PDPhB doped by iodine after relaxation for 16 h in unloaded state; (3) PDPhB containing iodine in 1.5 h after doping.

iodine concentration in the 5–30 wt % range. Although we have no information about the homogeneity of the iodine distribution in the doped samples, this factor seems to be insignificant for the interpretation of the effects observed, since all the doping methods mentioned in the experimental section give the same results within experimental error.

The consideration of the results obtained shows that the dependence of G on P and the largest values of conductivity, found in our experiments, are defined mostly by the structure of polymer molecules rather than by their supermolecular structure. This conclusion is supported by the slight change of conductivity during the compression of preliminarily pressed samples free of iodine and by the coincidence of σ dependences on P for homogeneously doped tablets and sandwich systems of "polymer–iodine–polymer" type. The latter circumstance also indicates that charge transfer complexes, which, in principle, can be formed during the doping of the studied polymers, do not play the decisive role in the mechanism of electrical conductivity under HP.

Changes in the band structure of a matrix as well as of a doping agent seem to be important for revealing the causes of the variations of electrophysical properties of doped conjugated polymers during their compression. As is known,[9] iodine transition into the high-conducting state is followed by the overlapping of its valence and conducting bands. On the other hand, the forbidden energy gap of conjugated systems becomes narrower under HP.[10] As a result, during compression the pattern of energetic bands at the interface between particles of iodine and polymer will greatly differ from that under atmospheric pressure. That is why under the conditions of HP one can expect rather specific surface phenomena at the "iodine–polymer" contact. Particularly, it cannot be excluded that under such conditions electron injection from iodine particles in the high-conducting state to the conduction band of polymer matrix takes place. In addition, the mobility of current carriers in the conduction band of a polymer is large because of favorable conditions for intermolecular conjugation realized under HP.[3,4] Thus, in the framework of a proposed mechanism, the effect of HP leads both to the increase of electron concentration and of their mobility. As a consequence, the increase in electrical conductivity of polyconjugated systems doped by iodine is observed during their compression. As far as the changes of the dielectric constant value under HP conditions are con-

cerned, they may be caused by the formation of a space charge at the interface of iodine particles with a polymer matrix.   However, to make final conclusions regarding the mechanism of the phenomenon discovered, some additional researches, which are in progress now, are necessary.

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