Molecular-dynamic simulation of conformations of acrylic monomers

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SUMMARY: The computer simulation of local dynamics of associates of homologous series of acrylic esters has been developed. It is shown that dynamic behaviour of molecules in associate intrinsically changes in different temperature regions. Solid-like behaviour is observed at low temperature, liquid-like at intermediate temperatures and gas-like behaviour at high temperature. Good correlation is obtained between the energy of intermolecular interactions of associates and melting points of corresponding chemical substances.

The computer modeling of structured liquids allows to clear the important details of associative structures, arising in them, mechanisms of intermolecular interaction and features of their local dynamics$^{1)}$.

The purpose of the present work was the computer modeling of local structure and dynamics of associates of acrylic acid and its saturated esters. Acrylic copolymers have the expressed properties of physical gels$^{2)}$. The theoretical research of such systems within the framework of statistical physics allows to describe general laws of their behaviour during deformation and interaction with a solvent $^{3)}$, however it does not allow to estimate the detailed structure and dynamical behaviour of distinct associates. It manages to be made by the method of molecular dynamics using detailed molecular models.

In the present work the atom-atom scheme for describing intramolecular and intermolecular interactions was used as for exploring the structure of associates in the minimum of potential energy, as for leading molecular-dynamic calculations$^{4,5)}$. The total potential energy E of molecules that form the associate in the framework of molecular mechanics can be described by the following sum of interactions:

$$E = E_b + E_\theta + E_{b\theta} + E_\phi + E_{nb} \qquad (1)$$

The terms in the right part of the equation present consequently the energy of stretching of valence bonds E_b, the energy of deformations of valence angles E_θ, the correction, connected

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with changing of the length of bonds during the changing of valence angles $E_{b\theta}$, the torsion energy E_{ϕ} and the non-bonded energy E_{nb}. The last term includes the van der Waals interactions and electrostatic interactions.

The algorithm of optimization using block - diagonal method was applied to find a configuration of molecules with the minimum of potential energy. After the minimization process, the potential energy of one isolated molecule (E_{S1}), molecules in the associate (E_{SA}) and the energy of intermolecular interaction (IMI) per one molecule (E_{IMI}) in the associate were calculated:

$$E_{IMI} = \frac{nE_{S1} - E_{SA}}{n} \qquad (2)$$

where n – the number of molecules in the associate.

In Fig. 1 the energy of intermolecular interactions (2) as a function of n for explored substances is shown. According to data, the IMI energy is growing by the increasing the number of molecules in the associate. But gradually this process is going down and E_{IMI} aspires to values respective the condensed condition for given substances. The monotonic character of dependencies attests that even for associates of near twenty molecules we can make a conclusion about energies of intermolecular interactions of respective substances. The data on Fig 2 can be the illustration to that fact, where the correlative dependence between the calculated values of E_{IMI} of associates of 16 molecules of saturated esters of acrylic acid and the melting point temperature of respective substances is shown.

During molecular dynamics computations the Beeman algorithm$^{6)}$ for integrating Newton's equations of motion, was used to compute new positions and velocities of each atom at each step to simulate the movement of atoms. By the integration of equations of motion with periodic renormalization of atom's velocities, the system relaxation was carried through for the given temperature before the condition in which the fluctuation of temperature did not outreach 2-3K. The time of thermal relaxation of the system for the explored molecules did not exceed 20 ps. After that average conformation characteristics of associates were calculated by means of calculating average distances between the chosen atoms of different molecules that form the associate in the period of 100 ps. In particular, the average distances between last carbon atoms in the double bonds, between atoms of oxygen and hydrogen of carboxyl groups and last carbon atoms of hydrocarbon radicals for esters of acrylic acid were calculated.

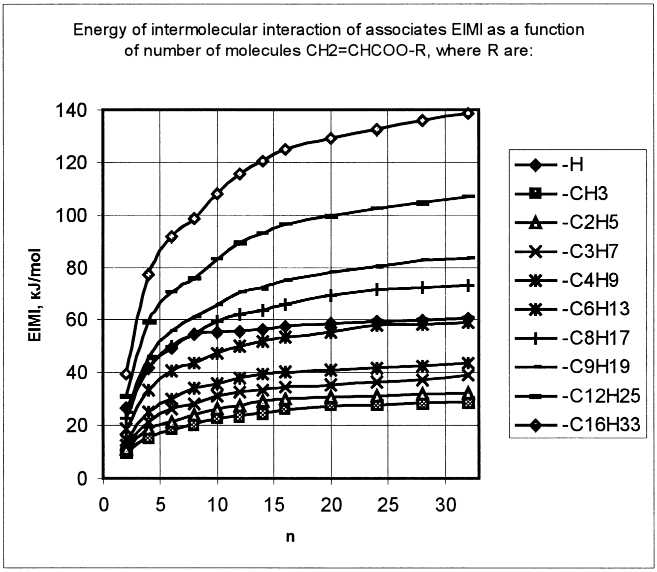


Fig.1: The energy of intermolecular interactions of associates of acrylic acid and its saturated esters as a function of number of molecules in the associate.

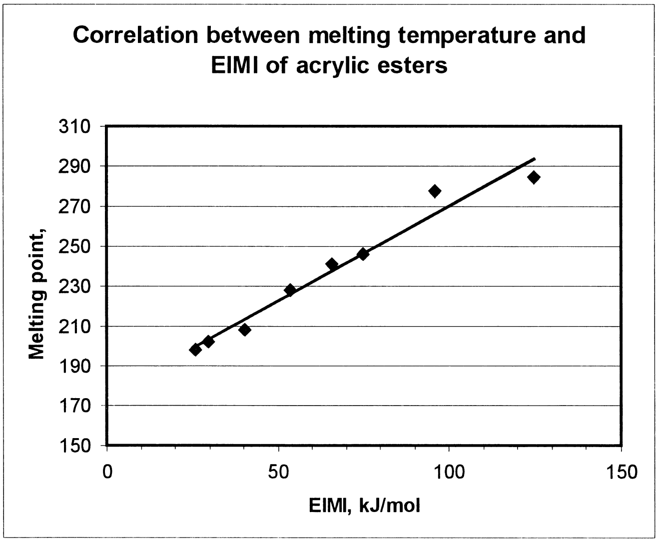


Fig. 2: Correlation between melting temperature and E_{IMI} of 16 molecules associates of acrylic esters.

The analysis of mechanism of local molecular motion of associate in molecular-dynamic experiment shows us that in different temperature diapasons the character of motion changes intrinsically (Fig.3). In the case of low temperature the associate of acrylic acid has conformation close to flat corresponding with minimum of potential energy. The fluctuation of angles and distances between atoms of different molecules is rather small. This associate case we can on probation call solid-like or crystal-like. By increasing the temperature, fluctuations of interatomic distances and angles in the associate begin to grow, though average values of interatomic distances change a bit. Hereby in spite of average conformations of associate comes near the conformation in the minimum of potential energy the "instantaneous" conformations prove highly far from it. The molecules begin to move respectively each other rather freely and the only fact of existing of the associate is saved. This condition lies in rather wide diapason of temperature. We can on probation call it liquid-like condition. By the next increasing of temperature, the stability of associate begins to destroy: molecules that form the associate fly to infinity even before the thermal balance or nearly after it during the period of under 50 ps. This associate condition we can probably call gas-like condition.

The existence of different conditions of thermal molecular motion of associate displays also on thermal dependence of correlation of distances between different groups of atoms in the associate. At low temperature correlation is rather high. This acknowledges the character of motion of the associate as solid-like. By the way to the liquid-like condition the coherency of motion of different groups of atoms disappears and the correlation between distances of different groups of atoms no longer differs from null.

The numerical modeling of dynamics of acrylic monomers allows understanding the reason of abnormal features in kinetics of polymerization, connected with the associative liquid structure. So, in particular it is known that during radical polymerization the connection of a radical with the double bond of growing chain is strictly spatially regulated. Therefore this monomers are characterized with high steric factor. On the first sight the true reactionary ability of monomers should decrease at transition from lowest to highest acrylates. Actually, however, all is on the contrary: the constant of speed of radical polymerization at transition from butylacrylate (BA) to nonylacrylate (NA) does not decrease, but considerably grows. Moreover, the small additive of BA in NA sharply reduces its reactionary ability.

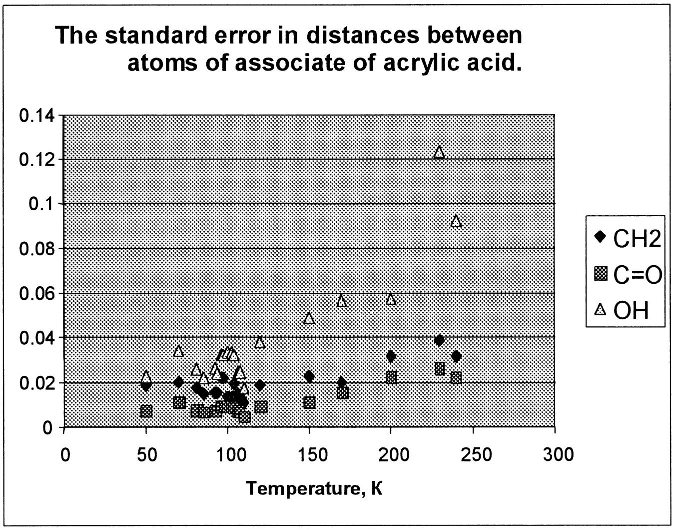
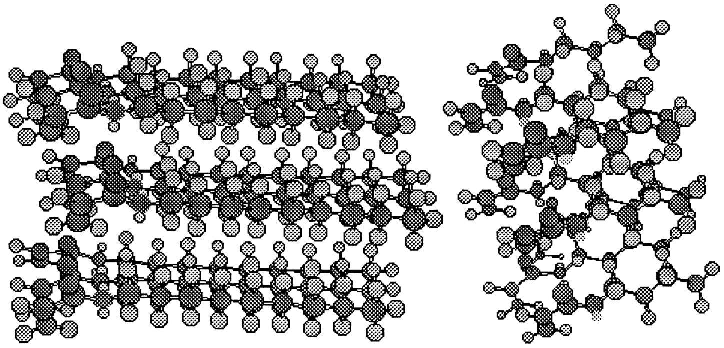


Fig. 3: Thermal dependence of the standard error of distances between different groups of atoms in associate of acrylic acid.

The reason of these anomalies, on our sight, consists in various associative structures of these monomers. Long hydrocarbon radical of NA stabilizes the associate and limits by that the mobility of double bonds in most favorable conformations for continuation of the kinetic chain. This is not the case for BA, which energy of van der Waals interactions of hydrocarbon fragments proves insufficient for the great limitation of rotational and translational mobility of molecules. As the result, its associative structure has less dense character and molecular mobility appears considerably higher. This illustrated by the associative structure in the minimum of potential energy (Fig 4) and can be described by thermal dependencies of average distances between carbon atoms at the double-bond, calculated on the base of molecular-dynamic experiments (Fig 5).



a) b)

Fig. 4: Structure of 9 molecules associates of NA (a) and BA (b) in the minimum of potential energy.

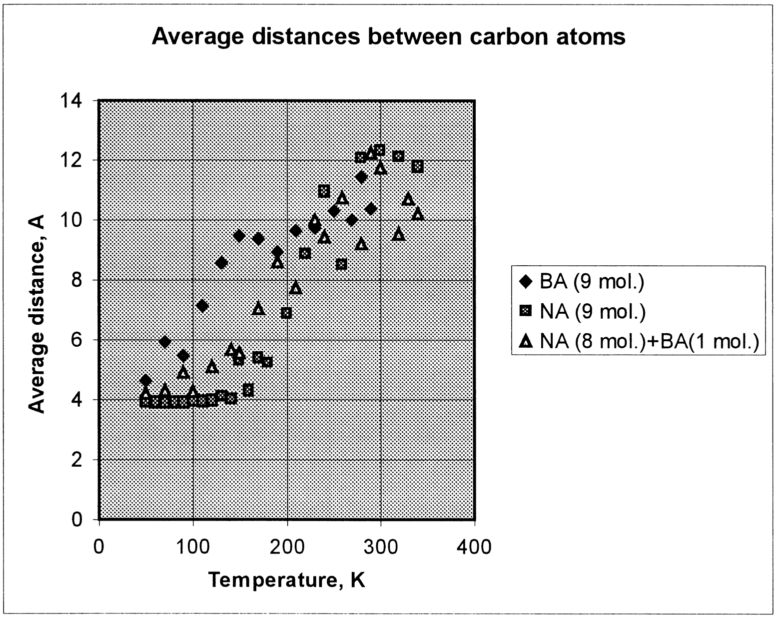


Fig.5: Average distances between carbon atoms as a function of temperature of 9 molecules associates.

Thus the numerical simulation let us open the relation between the peculiarities of molecular structure of monomers for synthetic polymers and their physical internal. The energy and the geometry of intermolecular interactions define the mechanisms of local molecular motion of monomers that are forming the associative structure. The energy of intermolecular interactions and molecular mobility change non-droningly in homologous series of saturated esters of acrylic acid.

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