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Abstract

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ON CERTAIN REGULARITIES IN THE CHANGE OF MELTING TEMPERATURE IN HOMOLOGOUS SERIES OF HETEROCHAIN POLYMERS

The question of the relation between the structure of polymers and their properties is of great interest and is the subject of numerous investigations.

We previously noted the existence of a relation between the melting temperature and the structure of the polymer chain in a series of heterochain polyamides with an even number of methylene groups in the repeat unit ([1]). This dependence between the melting temperature and the ratio of amide and methylene groups is expressed by the equation $y = 7x + 110$, where y is the melting temperature and x is the ratio of amide and methylene groups in mole percent. The existence of a graphical dependence between melting temperatures and the number of atoms in the repeat unit for polyamides was also noted by Champetier and Elion ([2]) and by Hill and Walker ([3]).

A more careful examination of this question, subsequently carried out by us, showed that a linear dependence exists not only in the series of even polyamides, but also in other series of heterochain polymers. To this end we examined homologous series of polyureas, polyamides, polyurethanes, polyesters, and polyanhydrides. It turned out that in all these series there is a quite definite dependence between the number of methylene groups in the repeat unit and the melting temperatures of the polymers. We selected especially detailed material on polyamides ([4]); the remaining classes of compounds were touched upon more briefly—only in order to show that the questions under consideration have general significance for all classes of heterochain polymers.

The similarity among the various types of polymers indicated above proved to go so far that, when the dependence between the melting temperature and the heterochain characteristic is represented graphically (the heterochain characteristic is the ratio of the number of heterobonds in the repeat unit to the number

Figure 1: Change in melting temperatures

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of methylene groups, in percent ([5])), it was found that all the lines on the graph intersect the ordinate axis at one point.

As can be seen from Fig. 1*a*, in each series the experimental points lie well on a straight line. Thus, in each series of similarly constructed polyamides, as well as in other classes of compounds to be considered by us below, there is a linear dependence between the melting temperature and the heterochain characteristic. The angle of inclination of the lines expressing the dependence of the melting temperature on the heterochain characteristic thus varies depending on the structure of the repeat unit. In the series of polyamides, the greatest angle of inclination is shown by polyamides obtained from acids and diamines with an even number of methylene groups in the molecule. It is interesting to note that it is not immaterial whether the odd number of methylene groups is in the diamine or in the dicarboxylic acid. In the case where we have dicarboxylic acids with an even number of methylene groups and diamines with an odd number, the angle of inclination of the corresponding straight line is greater than in the case where we have polyamides obtained from dicarboxylic acids with an odd number of methylene groups and diamines with an even number of methylene groups in the molecule. The smallest angle of inclination is shown by polyamides,

obtained from dicarboxylic acids and diamines with an odd number of methylene groups in the molecule.

In Fig. 1b, data are presented that were obtained for polyurethanes, polyureas, and polyanhydrides. Here we also observe a linear dependence between the melting temperatures in the homologous series of the indicated polymers and the magnitude of their heterochain characteristic, while the slope of the lines

Fig. 1. Change in melting temperatures in the series: 1 —polyureas, 2 —polyamides with an even number of CH_2 groups in the diamine and acid, 3 —the same according to refined data, 4 —polyamides from diamines with an even and acids with an odd number of CH_2 groups, 5 —polyamides from diamines with an odd and acids with an even number of CH_2 groups, 6 —polyamides from diamines and acids with an odd number of CH_2 groups, 7 —polyurethanes, 8 —polyanhydrides with an even number of CH_2 groups in the repeat unit, 9 —polyesters from glycols and acids with an even number of CH_2 groups, 10 —the same with an odd number of CH_2 groups in the acid, 11 —polyanhydrides with an odd number of CH_2 groups in the repeat unit.

upon passing from polyureas to polyurethanes and to polyanhydrides changes sharply: whereas in the first two classes of compounds an increase in melting temperatures is observed with increasing heterochain characteristic, in polyanhydrides the opposite picture occurs—with increasing heterochain characteristic the melting temperature decreases.

A similar dependence is also observed in the case of polyesters, as is evident from the graph shown in Fig. 1c; moreover, in the case of polyesters there are also differences between polyesters from dicarboxylic acids with an even number of methylene groups and polyesters obtained from acids with an odd number of methylene groups in the molecule.

In the case of polyesters, as in the case of polyanhydrides, the melting point decreases with increasing heterochain characteristic, in contrast to polyamides, polyurethanes, and polyureas, where the opposite dependence occurs. Apparently, this difference between polyesters and polyanhydrides, on the one hand, and all polymers containing nitrogen in the chain, on the other, is determined by the fact that amide groups, owing to their ability to form hydrogen bonds, when accumulated in the molecule increase the strength of the bonds between individual chains, which is expressed in an increase in the melting point. Conversely, polyesters and polyanhydrides, which have ether oxygen bonds, lower the melting points as the heterochain characteristic increases, i.e., as simple ether bonds accumulate in the chain. A simple ether bond is a factor that "softens" the structure of the chain, and the accumulation of simple ether bonds leads to a lowering of the melting point in the series of polyesters and polyanhydrides.

We have compiled equations for each of the groups of compounds considered; these are collected in Table 1. These equations were obtained in the usual way for the case of a straight line passing through two given points. As is known, in this equation the coefficient of x represents the tangent of the angle of inclination of the line to the abscissa axis, and the constant term represents the point of intersection of the line with the ordinate axis. As is seen in Fig. 1a–c, the experimental points fit sufficiently well on the corresponding straight lines constructed according to the equations given in Table 1.

Table 1

Equations for various polymers

No.	Polymer group	Equation
1	Polyamides with an even number of methylene groups in the unit	$y = 7x + 110$
2	Same	$y = 7x + 125^*$
3	Polyamides from a dicarboxylic acid with an odd number and diamines with an even number of methylene groups	$y = 6.2x + 110$

No.	Polymer group	Equation
4	Polyamides from dicarboxylic acids with an even number and diamines with an odd number of methylene groups	$y = 5.6x + 110$
5	Polyamides from dicarboxylic acids and diamines with an odd number of methylene groups	$y = 4.5x + 110$
6	Polyamides with sulfide sulfur in the chain	$y = 3x + 110$
7	Polyamides with ether oxygen in the chain	$y = 1.9x + 110$
8	Polyureas with an even number of methylene groups in the unit	$y = 8.4x + 110$
9	Polyurethanes with an even number of methylene groups in the unit	$y = 3.5x + 110$
10	Polyanhydrides with an even number of methylene groups in the unit	$y = -2.5x + 110$
11	Polyanhydrides with an odd number of methylene groups in the unit	$y = -3.6x + 110$
12	Polyesters with an even number of methylene groups in the unit	$y = -3.0x + 110$
13	Polyesters with an odd number of methylene groups in the unit	$y = -3.6x + 110$

* For the case when the melting point was determined dilatometrically.

The slope of the straight lines varies depending on the nature of the hetero bond. The greatest slope is possessed by the line for polyureas. These are followed by polyamides, first with an even number of methylene groups, and then with various combinations of odd-numbered units. After this come polyurethanes, and then polyamides containing sulfide sulfur and a simple ether linkage in the macromolecular chain.

The second group of compounds, in which the tangent of the slope angle has a negative value, includes, in sequence, polyanhydrides with an odd number of methylene groups, polyesters with an even number of methylene groups in the unit, and polyesters and polyanhydrides with an odd number of methylene groups in the unit.

It is interesting to note that the lines for the last two compounds merge, and the points corresponding to them fit well on a single straight line. It should be said that we selected—especially in the polyester and polyanhydride series—compounds in which the heterochain characteristic had an average value, since in the polyester series, at large values of the heterochain characteristic, the absence of such a smooth regularity is observed, apparently associated with polar effects caused by the large number of carbonyl groups in the molecule of these polyesters.

As can be seen from the graph shown in Fig. 1 , all the lines expressing the dependence of melting temperatures on the heterochain characteristic intersect the ordinate axis at one point, at 110°, i.e., in the region corresponding to the melting temperature of polyethylene.

It should be noted that the magnitude of the intercept cut off on the ordinate axis strongly depends on the method of determining the melting temperature. Thus, curve 2, showing the dependence of melting temperatures in the series of even polyamides, was constructed on the basis of melting temperatures determined by the dilatometric method. In this case the melting temperatures are approximately 15° higher than usual, and therefore the intersection of this curve with the ordinate axis is not at 110°, but at 125°.

The fact that the point of intersection of the curve with the ordinate axis does not fully correspond to the generally accepted melting temperature of polyethylene is easy to understand if one takes into account that the latter in general has no exact melting temperature. According to various data, it varies within a rather broad interval. The width of this interval and its position depend both on the method of determining the melting temperature and on the nature of the polyethylene sample studied, its molecular weight, and other characteristics. Polyethylene obtained at high pressure has a melting temperature which, according to data from various authors, lies between 104 and 111° ([6], [7]), while that obtained at low pressure lies between 124 and 133° ([6], [7]), whereas polymethylene obtained by the decomposition of diazomethane melts at 128° ([8]).

Taking these circumstances into account, it must be acknowledged that there is fairly good agreement between the conclusions from the proposed equations and the experimental data.

The presence of a linear dependence of the melting temperatures of the groups of polymers considered by us on their heterochain characteristic shows that there is a direct relationship between the physical properties and the structure of these polymers.

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Note: Figure translations are in progress. See original paper for figures.