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Chapter 6

Some Features of the Chemical Plasticization of Polymers Without Side Groups



O. Manchenko , V. Nizhnik, O. Kuryliuk, N. Iukhymenko ,
and V. Budzinska 

Abstract The changes in the temperature of the glass transition (T_g), the energy of cohesion (E_{coh}), the modulus of elasticity when shifted (G) in the polyethers, which has difference in the polarity and the van der Waals volume (V_{vw}) of the links, were analyzed. Also, the phenomenon of chemical plasticization in polyether through introduction into the main chain of macromolecules of additional nonpolar groups was studied. It was shown that the criterion of chemical plasticization is written by the formulae $\Delta T_g = \text{const} \cdot \Delta V_{\text{vw}}$.

6.1 Introduction

The chemical plasticization of polymers lies in changing the chemical composition of macromolecules, which reduces the transition temperature of a polymer from a glass state to a high elastic state—the glass transition temperature (T_g) and is accompanied by a decrease in the values of some of its thermodynamic, electrical, physicochemical characteristics and viscosity.

In the work [1], it was shown that this type of plasticization is possible due to a decrease in the polarity of the macromolecules, the replacement of the side polar

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groups with less polar and nonpolar or rigid fragments of the macromolecule chains on the flexible ones. However, information on the features of chemical plasticization for different classes of polymers is limited.

6.2 Experimental

For heterochained polymers, the chains of which do not contain side groups, one of the methods of chemical plasticization is to reduce the polarity of the macromolecule links. For polyoxides and polyimines, the replacement of polar groups to nonpolar groups, for example, in the polyethylene oxide group $-O-$ with a dipole moment of 0.45 D, and in the polyethyleneimine the group $-NH-$ with a dipole moment of 0.4 D to the nonpolar group $-CH_2-$, leads to the loss of the polarity of the polymer and the dipole-dipole interaction of the links, which is typical for polymethylene. The temperature of the glass transition (T_g) and some characteristics of these polymers which have different chemical composition of the groups are given in Table 6.1. The values T_g and μ were taken from the work [2, 3]. Van der Waals volume of a polymer, assigned to the monomers, is calculated according to the formula $V_{\text{spec}}/V_{\text{VW}} = 1.55$, where $V_{\text{spec}} = M/\rho$ (M —molecular weight of the link, ρ —the density of the polymer). The energy of internal rotation (U_{ir}) around the valence bond were taken from work [4]. The energy of the cohesion of the link (E_{coh}) and of the methylene fragment with the number of valence bonds to the identical links of polar polymers is calculated by contributions to this energy of structural groups [2]. The Modulus of polymer displacement in an amorphous state, or its rigidity (G_a) was determined from the van Krevelen and Hovtitser empirical relation $G_a \approx \frac{3}{1 + \frac{600}{T_g}} 10^9 \text{ N/m}^2$, where G_a —rigidity of the polymer, T_g —the temperature of the glass transition (See Table 6.1).

Table 6.1 shows that when replacing polar groups in the links of polyethylene oxide and polyethyleneimine with correspondingly certain values of the dipole moment (μ) to the nonpolar methylene group, the forces of intermolecular adhesion (E_{coh}), are weakened, the segments become more flexible and movable (T_g —decreases), and the polymer has smaller elasticity (G_a —decreases). This corresponds to the phenomenon of plasticization. An increase in the van der Waals volume (V_{vw})—the space where the

Table 6.1 The value of T_g , volume, thermodynamic, electrical, elasticity characteristics and characteristics of polymer cohesion

Polymer	Link and methylene fragment	T_g , K	$V_{\text{vw}} \cdot 10^6$, m^3/mole	U_{ir} , kJ/mole	μ , D	E_{coh} , kJ/mole	$G_a \cdot 10^{-9} \text{ N/m}^2$
Polyethylene-oxide	$-CH_2-CH_2-O-$	206	26.4	3.2	0.45	15.1	0.66
Polyethyleneimine	$-CH_2-CH_2-NH-$	228	28.5	8.3	0.4	13.45	0.76
Polymethylene	$-CH_2-CH_2-CH_2-$	170	30.9	11.5	—	12.4	0.82

monomeric link is set, which can not penetrate other links with energy corresponding to normal temperatures, also agrees with this conclusion.

For selected polar polymers, in particular polyethylene oxide and polyethylenimine, T_g do not correlate with the values of their dipole moments. T_g of polyethylene oxide is lower than that of polyethylenimine, and its link is more polar than a link of polyethylenimine (the dipole moment of carbon bonds with other atoms is bigger, when the element is located at the right side of periodic system). The reason for a higher, compared to polyethylene oxide T_g of polyethylenimine is the bigger value of the internal rotational energy (U_{ir}) around the bond $-NH-$ compared with the bond $-O-$ (Table 6.1). This makes the chains of the polyethylenimine macromolecules less flexible than polyethylene oxide.

Another method of chemical plasticization of polar polymers without side groups is the introduction of additional nonpolar groups, in particular nonpolar groups $-CH_2-$, into the main chain of macromolecules. Such plasticization is illustrated by ethers with a growing number of nonpolar groups in the chain. Table 6.2 shows the values of T_g and some characteristics of polyoxides, the links of which are distinguished in the number of $-CH_2-$ groups (See Table 6.2).

Table 6.2 shows the values of T_g , which were obtained experimentally and calculated on group contributions in accordance with [2]. The values of T_g are fairly close. The charts of the dependence of experimentally and theoretically calculated T_g of polyoxides on the number of groups $-CH_2-$ in the link of the macromolecule and Van der Waals volume, referenced to the monomer unit, are shown in Figs. 6.1 and 6.2.

Table 6.2 The values of T_g , volume, elasticity characteristics and characteristics of the polyoxyethylene cohesion

	Link	T_g , K		$\rho_a \cdot 10^{-3}$, kg/m ³	$V_{vw} \cdot 10^6$, m ³ /mole	E_{coh} / bond, kJ/ mole	$G_a \cdot 10^9$, N/m ²
		exp	calc				
Polymethylene Oxide	$-CH_2-O-$	213	215	1.25	15.48	5.49	0.79
Polymethylene Oxide	$-(CH_2)_2-O-$	206	207	1.125	25.2	5.2	0.77
Poly(trimethylene Oxide)	$-(CH_2)_3-O-$	195	198	1.0	37.4	4.9	0.73
Poly Tetramethylene oxide	$-(CH_2)_4-O-$	185	192	0.98	44.6	4.6	0.71

Fig. 6.1 The dependence of the glass transition temperature T_g of polyoxides on the number of methylene groups along the chain of main valences within the monomer unit: the experimental values of T_g (1) and the theoretically calculated T_g (2)

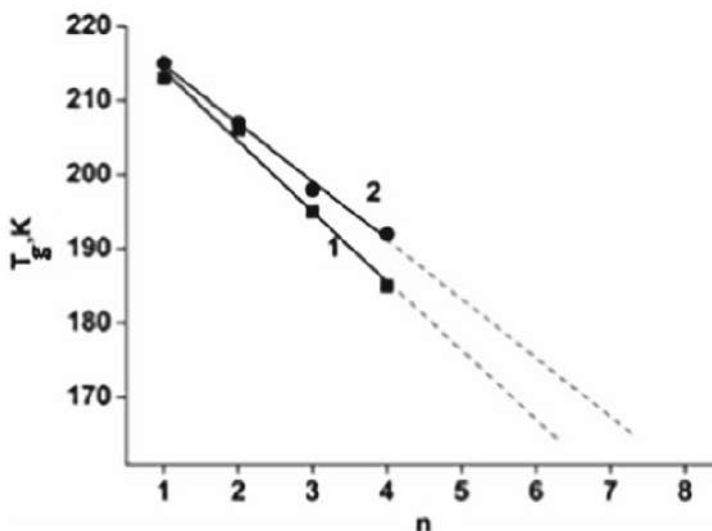
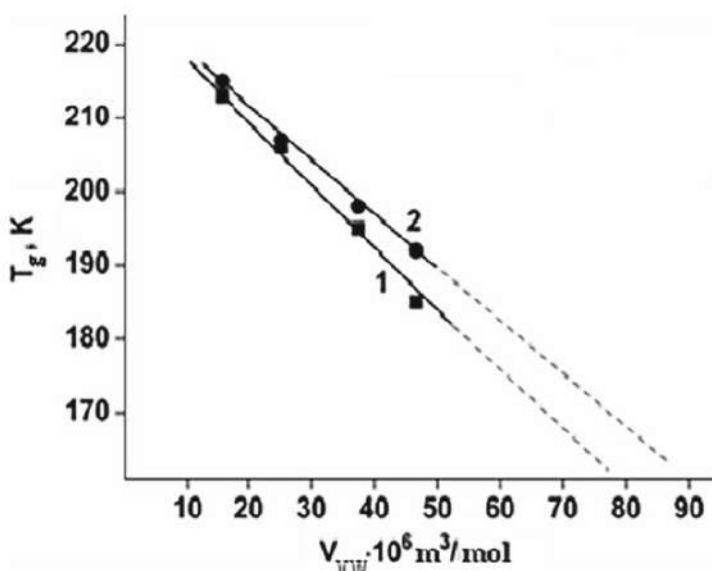


Fig. 6.2 The dependence of the glass transition temperature T_g of the polyoxides on the Van der Waals volume of the polymer calculated on the monomer link: the experimental values of T_g (1) and the theoretically calculated T_g (2)

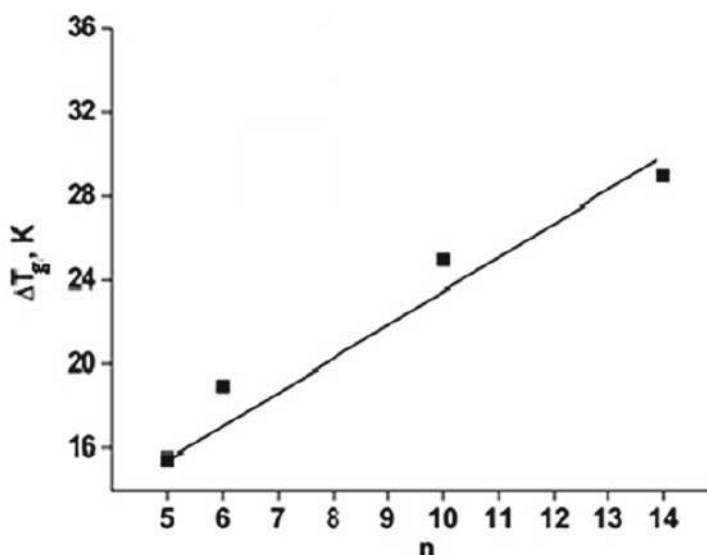


6.3 Results and Discussion

The chemical plasticization in this class of polymers is that the T_g decreases proportionally with the increase in the number of nonpolar groups in the polyoxide chain, as can be seen in Table 6.2 and Fig. 6.1. Extrapolation of this dependence on T_g of polymethylene (Table 6.1) shows that the influence of the polar group $-\text{O}-$ on the glass transition temperature disappears when the length of the nonpolar fragment reaches the polyoxide chain in 6 methylene groups.

The data in Table 6.2 and Fig. 6.2 show the linear dependence on T_g of polyoxide with different content of nonpolar groups $-\text{CH}_2-$ from the Van der Waals volume, assigned to the monomer link. The criterion for reducing T_g of polyoxides with this type of chemical plasticization is written as:

Fig. 6.5 The dependence ΔT_g of polyether on the number of $-\text{CH}_2-$ groups in the methylene fragment



of introduced nonpolar groups in the chain of the macromolecule is less distinct. This type of plasticization depends on the chemical nature of the polymer.

Polymformals can be considered as polymethylene oxide, in which in each of second group $-\text{CH}_2-$, changes on a methylene long fragment. This allows us to calculate the plasticization effect of the methylene fragment on the polymethylene oxide using the values T_g of polymethylene oxide and polyformals, and the plasticization effect of one methylene group of the fragment.

Figure 6.5 shows the dependence of the plasticization effect in polymethylene oxide from the number of nonpolar groups in the methylene fragment. The tangent of the angle of this dependence determines the contribution of the methylene group to the plasticization of the polyoxide. It is 1.5 K to the methylene group. This means that with sufficiently long methylene fragments, the influence of the nonpolar group on T_g of the polyoxide is small. A similar calculation of the contribution of the methylene group to the plasticization of polymethylene oxide at a small size of the methylene fragment from the data in Table 6.2 gives a significant contribution of the methylene group in plasticization, 6 K to the methylene group.

6.4 Conclusion

Thus, the chemical plasticization of simple polyethers by increasing the number of non-polar $-\text{CH}_2-$ groups in the chain of a macromolecule occurs effectively at a small size of the methylene fragment, when the polymer has a strong dipole-dipole interaction and these additionally introduced nonpolar groups significantly weaken this interaction. With the increase in the size of the methylene fragment, when the distance between the polar groups becomes bigger and the dipole-dipole interaction of the macromolecules weakens, the addition of new nonpolar groups does not

significantly change intermolecular interaction, since it mainly determines the weak forces of Van der Waals.

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