Viscoelastic Behavior of Some Di(normal alkyl) Phthalates

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The viscoelastic behavior of a homologous series of di-*n*-alkyl phthalates varying in alkyl chain length from methyl- to nonyl- was studied by means of torsional braid analysis (TBA). The glass transition temperatures, T_g, were determined as the temperature at loss maximum. The T_g decreases with increasing alkyl chain length in the di-*n*-alkyl phthalates, up to dibutyl. Thereafter, the T_g increases gradually with further increase in the alkyl chain length. This behavior can be explained by taking into account two factors which determine the T_g, the molecular weight and the intermolecular interaction. The increase in the number of methylene groups in the phthalates brings about two effects: first, the T_g is increased with increasing molecular weight and, second, the T_g is decreased owing to shielding of the interaction between polar carbonyl groups due to the presence of non-polar methylene groups. When the number of methylene groups is four, the two effects counterbalance each other and the T_g of dibutyl phthalate is the lowest of the di-*n*-alkyl phthalate series.

It is generally recognized that the glass transition temperatures (T_g) of polymers or oligomers can vary with the chain length, and a number of studies have been reported which are concerned with the relationship between the T_g and the molecular weight of polymers and, moreover, the factors affecting the dependence of the T_g on the molecular weight.[1-6] It may be pointed out that several factors affect the T_g-molecular weight relation: these include the crystallinity, the molecular weight distribution, the complexity of the backbone chain, such as the stiffness or flexibility, the polarity, and the end-group or chain association effect.[5,6,11] In spite of its importance, the mutual relation of these factors is not clear at present. In particular, it is likely that no attention was paid to the association effect caused by end-groups, since the effect is very slight compared with that of the molecular weight.[4] It is guessed that this end-group effect is appreciable only when the chain length is very short, that is, when the molecular weight is low. It is the purpose of the present work to clarify the effectiveness of the end-groups on the T_g-molecular weight relation.

However, the relaxation behavior of low molecular-weight glassy substances was more recently noted in analogy to that of polymers.[7-10] Secondary dispersions have already been observed for 1-alkanols and lactones, and were discussed in relation to the molecular motions of methylene sequences.[7-9] It is the aim of the present paper to report whether similar behavior due to methylene sequences appears in di-*n*-alkyl phthalates.

Experimental

Samples. The samples used in this study were various di-*n*-alkyl phthalates: dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPrP), dibutyl phthalate (DBP), dipentyl phthalate (DPeP), dioctyl phthalate (DOP), and dinonyl phthalate (DNP). These phthalates received from commercial souces were washed in water, dried on molecular sieves, and then distilled *in vacuo*. The conditions were as follows: DMP −132 °C/666 Pa, DEP −141 °C/666 Pa, DPrP −158 °C/666 Pa, DBP −182 °C/666 Pa, DPeP −170 °C/66.6 Pa, DOP −165 °C/13.3 Pa, DNP −184 °C/13.3 Pa.

Measurements. The viscoelastic behavior of di-*n*-alkyl phthalates was studied using the torsional braid analysis (TBA) method at a frequency of 0.5 Hz. After dipping a glass braid used as the supporting substrate into liquid samples, these sample-braid composite systems were mounted on the torsional pendulum apparatus, quickly immersed in liquid nitrogen, and then damping measurements were made for an increasing temperature rate of 0.5 °C/min.

Using the TBA method, the elastance of sample-glass braid composite system is obtained, and not the elasticity of the samples themselves. Since it was previously confirmed that the glass braid shows no dispersion in this temperature region, the observed dispersion behavior is considered to be due to the impregnating sample itself.[12,13]

Results and Discussion

The viscoelastic behavior of di-*n*-alkyl phthalates is shown in Figs. 1 and 2. The storage elastance rapidly decreases in the temperature region in which the maximum of the loss elastance occurs. For damping measurements, the glass transition temperature (T_g) is customarily taken as the temperature of maximum loss elastance. The T_g values, which lower than the melting points by 30—60 °C, are summarized in Table 1 together with the melting points of the phthalates. T_g determined using the DTA have been reported by Garfield and Petrie[14] to be −85 °C for diethyl phthalate and −87 °C for dioctyl phthalate. This is in good agreement with the present data, taking into account the frequency of 0.5 Hz of the present TBA method.[16]

In the case of dimethyl and dioctyl phthalates, the viscoelastic behavior differs somewhat from that of the other phthalates. In the present experiments, the samples were quickly cooled down to glass form and then the temperature was gradually raised. The storage elastance first decreases near the T_g value. A subsequent increase in storage elastance is observed and may be attributed to crystallization, because, generally speaking, substances can be crystallized only in the supercooled liquid state at temperatures between the T_g and the melting point. With further increase in the temperature the storage elastance finally decreases again due to fusion. The temperature of the final decrease in storage elastance approximately coincides with the melting

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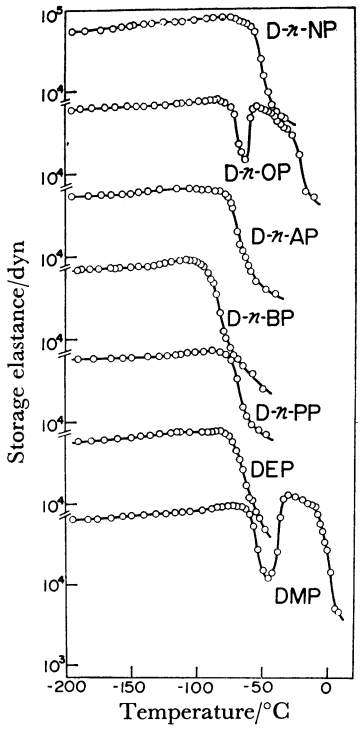


Fig. 1. Temperature dependence of storage elastance for di-*n*-alkyl phthalate-braid composite systems.
D-*n*-NP: di-*n*-nonyl phthalate, D-*n*-OP: di-*n*-octyl phthalate, D-*n*-AP: di-*n*-amyl phthalate, D-*n*-BP: di-*n*-butyl phthalate, D-*n*-PP: di-*n*-propyl phthalate, DEP: diethyl phthalate, DMP: dimethyl phthalate.

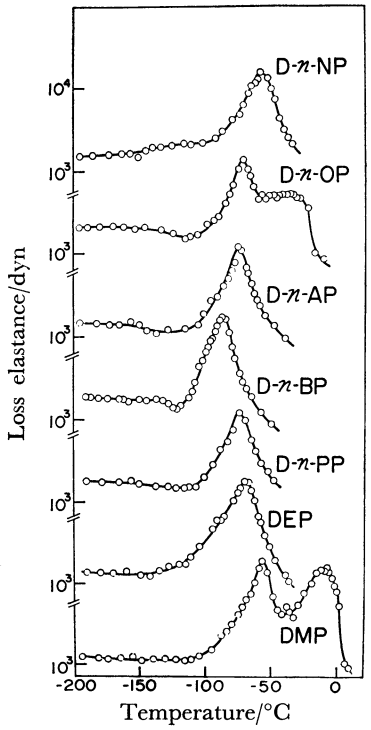


Fig. 2. Temperature dependence of loss elastance for di-*n*-alkyl phthalate-braid composite systems.
D-*n*-NP: di-*n*-nonyl phthalate, D-*n*-OP: di-*n*-octyl phthalate, D-*n*-AP: di-*n*-amyl phthalate, D-*n*-BP: di-*n*-butyl phthalate, D-*n*-PP: di-*n*-propyl phthalate, DEP: diethyl phthalate, DMP: dimethyl phthalate.

Table 1. Glass transition temperatures and melting points of the di-*n*-alkyl phthalates studied

Substance	T_g / °C		T_m [b] / °C
	TBA method	DTA method[a]	
Dimethyl phthalate	−57	—	0 or 5.5[c]
Diethyl phthalate	−69	−85	−40.5 or 40[c]
Dipropyl phthalate	−75	—	−31
Dibutyl phthalate	−84	—	−35 or −40[c]
Dipentyl phthalate	−75	—	—
Dioctyl phthalate	−70	−87	−25
Dinonyl phthalate	−60	—	—

a) Quoted from Ref. 14. b) Melting points quoted from Ref. 15. c) Two data are reported.

point of −25 °C for dioctyl phthalate and of 0 °C for dimethyl phthalate. Corresponding to the above-mentioned behavior, the loss elastance *vs.* temperature curves show two maxima. The other phthalates may not crystallize as do the dioctyl and dimethyl phthalates, and each shows a single dispersion due to the glass transition.

It is well established that the T_g of polymers becomes higher with increasing molecular weight.[1-3] Recently, Cowie has studied the dependence of the T_g on the molecular weight for a number of oligomers and polymers.[6] The change in T_g with increasing molecular weight is more marked in the oligomeric region than in the polymeric region.

Figure 3 shows the T_g values of di-*n*-alkyl phthalates as a function of the alkyl chain length, ***n***. Compared with the case of usual polymers or oligomers, the change in the T_g with chain length is particularly interesting in the case of the di-*n*-alkyl phthalate series. The T_g decreases with increasing alkyl chain length up to dibutyl. Thereafter, the T_g increases gradually with a further increase in the alkyl chain length. This behavior is not satisfactorily explained by the conventional concept of the T_g-molecular weight relation. It is necessary to consider that there exist two factors which determine the T_g: (1) the molecular weight or chain length and (2) the intermolecular interaction. The increase in the number of methylene groups in the di-*n*-alkyl phthalates brings about two effects: first, the T_g becomes higher with increasing molecular weight and, second, the T_g decreases due to shielding of the interactions between the polar carbonyl groups and/or the aromatic rings due to the presence of non-polar methylene groups. When the number of methylene groups is four, the two effects counterbalance each other and the T_g of the dibutyl phthalate is the lowest of the di-*n*-alkyl phthalate series.

Figure 3 also shows the two sets of series of T_g *vs.* alkyl chain length plots for 1-alkanols[9] and lactones.[8] In this case, each has a different polar end-group, one having an –OH group and the other a –COO– group, respectively. An identical trend is also observed for

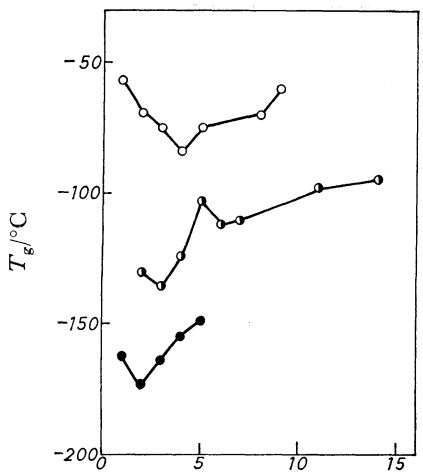
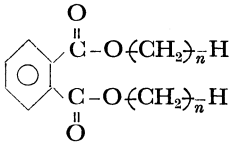
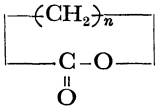


Fig. 3. Glass transition temperature T_g of di-*n*-alkyl phthalates, 1-alkanols,[9] and lactones[8] as a function of n, where n is the number of methylene groups.
○: Di-*n*-alkyl phthalates.



◑: Lactones.[8]



●: 1-Alkanols.[9]

$$H\{CH_2\}_{\overline{n}}OH$$

these two series. In the 1-alkanol series, a pronounced minimum T_g value is observed for ethyl alcohol, that is, $n=2$. On the other hand, in the lactone series, the minimum T_g value is situated at $n=3$, that is, γ-butyrolactone.

It is believed that the n-value which shows the minimum T_g value in a given series having methylene groups depends on the mutual interaction strength of the end-groups. The stronger the interaction between the attractive groups in molecules, the larger the n-value, since longer methylene sequences are required in order to shield the attractive force which brings about a higher T_g. Such a concept appears to be reasonable from the results shown in Fig. 3.

With regard to the secondary dispersions of low molecular-weight substances, several investigators have observed dispersions at temperatures below the T_g for 1-alkanols,[7,9] lactones,[8] glucose pentaacetate, *etc.*[10] Some were not observed in dielectric loss measurements and were assigned to molecular motions of alkyl chains. However, for the di-*n*-alkyl phthalates reported here, no secondary dispersion was observed at all, as is shown in Fig. 2. Further experiments on other systems will be necessary in order to elucidate this very interesting problem.

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