

Structural Dependence of Density in High Molecular Weight Esters

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The effect of molecular structure on density has been examined in high molecular weight esters (molecular weight 300-900), having varying degrees of branching. Densities were calculated from an empirical equation, which agrees well with the experimental values (error $\pm 1.5\%$), irrespective of branching. Since density is related to molecular packing and hence to the molecular rotation, in *n*-alkanes, the glass transition temperature (T_g) and density both increase with molecular weight, and hence T_g is directly related to the density. The esters exhibit a complex behavior. In linear esters the T_g decreases with molecular weight which is explained from group contribution and molecular interactions. In the \pm -branched esters, however, T_g decreases with molecular weight until the molecular weight reaches 600 and increases sharply thereafter. The Y-branched esters show an intermediate behavior. The dependence of T_g on molecular weight has been explained from the segmental motion.

Introduction

Long-chain esters (molecular weight 300-2000) are generally used as plasticizers in polymers (1). A systematic study of the macroscopic liquid-state properties such as the dependence of molecular weight and molecular structure helps in the proper selection of the plasticizers and also in understanding their plasticizing mechanism (2-5). Such an investigation would be immensely profitable as the liquid-state behavior of long-chain molecules beyond a molecular weight of 400 is hitherto unknown. Density (ρ) is a very useful bulk property of a liquid, and these data in the form of molar volume and specific volume ($1/\rho$) enable us to learn the molecular characteristics, especially their internal flexibility. We have measured the densities of long-chain esters as a function of both molecular weight and branching besides predicting the density data from an empirical equation imbibing their structural features (6). Since the densities reflect the nature of the packing and hence the flexibility, it seems logical that it may be related to the glass transition behavior of these liquids. We have attempted to correlate the densities with the glass transition of these liquids.

In the present investigation, the effect of molecular weight and structure on the densities of a homologous series of esters, namely, dialkyl sebacate ester (DSEs) and 1,10-decanediol diester (DDEs), which are linear, flexible molecules, triglycerides (TGEs) and 2-(hydroxymethyl)-2-methyl-1,3-propanediol trialkyl esters (TTEs), which are Y branched, compact molecules, and pentaerythritol tetraalkyl esters (PTEs) which are \pm branched and highly compact rigid molecules, has been studied.

Experimental Section

The structures and molecular weights of DDEs, TTEs, and PTEs are given in Tables I-III, and those for the other two series, DSEs and TGEs, along with their preparation are given elsewhere (7). The esters DDEs, TTEs, and PTEs were prepared by reacting 1,10-decanediol, 2-(hydroxymethyl)-2-methyl-1,3-propanediol, and pentaerythritol with respective acid chlorides in toluene using pyridine for removing HCl. The esters were separated from the reaction mixture by fractional distillation and were purified by vacuum distillation while solids were purified by recrystallization. These esters were characterized by ^1H NMR and IR spectra and were found to be pure within the sensitivity of these measurements.

The densities of DSEs and TGEs ester series are given elsewhere (6, 8). For other ester series, densities were measured by using a mercury-calibrated dilatometer (9) in the temperature range 303-413 K. The dilatometer consisted of a 10-mL capacity bulb, to which a long capillary tube was attached. The liquid sample was charged into the dilatometer by means of a hypodermic syringe having an extended needle which could fill the tube through the bottom of the bulb without wetting the capillary tube. Similarly, powder samples were introduced through a long capillary funnel. After the weight of the sample was determined to the nearest 0.1 mg in air, a glass stopper was placed at the top of the dilatometer which was then immersed in a constant silicone oil bath in its normal upright position. The change in the volume of the dilatometric liquid was measured from the height of the liquid meniscus in the capillary tube viewed through a cathetometer. The densities were measured at different temperatures from the rise in the height of the liquid in the capillary tube which was calibrated earlier with mercury whose density was obtained from international critical tables.

The volume of the liquid sample (\bar{V}_T) at a desired temperature (T) was computed by substituting the previously known values of \bar{V}_0 , S_T , l_T , and l_0 into the following empirical equation:

$$\bar{V}_T = \bar{V}_0 + S_T(l_T - l_0) \quad S_T = \left(\frac{\alpha - \beta}{\alpha}\right) A$$

where \bar{V}_0 and l_0 are the volume and height, respectively, of mercury at T ($^\circ\text{C}$), l_T is the height of the liquid at T ($^\circ\text{C}$), α and β are the coefficients of thermal expansion of mercury and glass, respectively, and A is a constant which was obtained from the slope of the plot of the volume of mercury as a function of the height of mercury in the capillary at different temperatures. It may be noted that the above empirical equation is applicable only when the dilatometer calibrations and volume measurements are carried out at the same temperature.

Finally, the densities of the liquids at the relevant temperature were computed from their weights in air, and their volumes determined by dilatometric methods; i.e.

$$\text{density in air} = \frac{\text{wt of sample in air/g}}{\text{obsd vol/mL}}$$

All the density values of the esters were corrected for air buoyancy (10); the data are given in Tables IV-VI. The error involved in density measurements is $\pm 0.2\%$.

Table I. Structure and Molecular Weights of DDEs

$$\text{CH}_3-(\text{CH}_2)_x-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_{10}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_x-\text{CH}_3$$

<i>x</i>	name	abbreviation	empirical formula	molecular weight
2	1,10-decanediol dibutyrate	DDB	C ₁₈ H ₃₄ O ₄	314
6	1,10-decanediol dioctanoate	DDO	C ₂₆ H ₅₀ O ₄	426
8	1,10-decanediol didecanoate	DDD	C ₃₀ H ₅₈ O ₄	482
14	1,10-decanediol dipalmitate	DDP _a	C ₄₂ H ₈₂ O ₄	650

Table II. Structure and Molecular Weights of TTEs

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2-\text{O}-\text{C}-(\text{CH}_2)_x-\text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_x-\text{CH}_3 \\ | \\ \text{O} \\ \parallel \\ \text{CH}_2-\text{O}-\text{C}-(\text{CH}_2)_x-\text{CH}_3 \end{array}$$

<i>x</i>	name	abbreviation	empirical formula	molecular weight
1	2-(hydroxymethyl)-2-methyl-1,3-propanediol tripropionate	TMEP	C ₁₄ H ₂₄ O ₆	288
2	2-(hydroxymethyl)-2-methyl-1,3-propanediol tributyrate	TMEB	C ₁₇ H ₃₀ O ₆	330
3	2-(hydroxymethyl)-2-methyl-1,3-propanediol trivalerate	TMEV	C ₂₀ H ₃₆ O ₆	372
5	2-(hydroxymethyl)-2-methyl-1,3-propanediol triheptanoate	TMEH	C ₂₆ H ₄₈ O ₆	456
6	2-(hydroxymethyl)-2-methyl-1,3-propanediol trioctanoate	TMEO	C ₂₈ H ₅₄ O ₆	498
7	2-(hydroxymethyl)-2-methyl-1,3-propanediol trinonanoate	TMEN	C ₃₂ H ₆₀ O ₆	540
8	2-(hydroxymethyl)-2-methyl-1,3-propanediol tridecanoate	TMED	C ₃₅ H ₆₆ O ₆	582
14	2-(hydroxymethyl)-2-methyl-1,3-propanediol tripalmitate	TMEP _a	C ₅₃ H ₁₀₂ O ₆	834

Table III. Structure and Molecular Weights of PTEs

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2-\text{O}-\text{C}-(\text{CH}_2)_x-\text{CH}_3 \\ | \\ \text{CH}_3-(\text{CH}_2)_x-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}_2\text{C}-\text{C}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_x-\text{CH}_3 \\ | \\ \text{O} \\ \parallel \\ \text{CH}_2-\text{O}-\text{C}-(\text{CH}_2)_x-\text{CH}_3 \end{array}$$

<i>x</i>	name	abbreviation	empirical formula	molecular weight
0	pentaerythritol tetraacetate	PETA	C ₁₃ H ₂₀ O ₈	304
1	pentaerythritol tetrapropionate	PETP	C ₁₇ H ₂₈ O ₈	370
2	pentaerythritol tetrabutyrate	PETB	C ₂₁ H ₃₆ O ₈	416
3	pentaerythritol tetravalerate	PETV	C ₂₅ H ₄₄ O ₈	472
5	pentaerythritol tetraheptanoate	PETH	C ₃₃ H ₆₀ O ₈	584
6	pentaerythritol tetraoctanoate	PETO	C ₃₇ H ₆₈ O ₈	640
7	pentaerythritol tetranonanoate	PETN	C ₄₁ H ₇₆ O ₈	696
8	pentaerythritol tetradecanoate	PETD	C ₄₅ H ₈₄ O ₈	752

Table IV. Densities of 1,10-Decanediol Dialkyl Esters

<i>T/K</i>	$\rho / (\text{kg m}^{-3})^a$			
	DDB	DDO	DDD	DDP _a
303	940.9 (942.3)	903.4 (914.2)		
313	933.8 (933.3)	897.1 (906.2)		
323	926.5 (924.6)	890.1 (898.5)	887.9 (890.2)	
333	918.7 (916.0)	883.5 (890.7)	881.3 (882.8)	
343	911.3 (907.5)	876.8 (883.2)	874.0 (875.5)	
353	904.4 (898.8)	869.7 (875.5)	866.9 (868.1)	845.0 (853.9)
363	896.6 (890.4)	862.6 (868.0)	860.7 (860.9)	838.9 (847.2)
373	888.9 (881.9)	855.9 (860.5)	854.3 (853.6)	832.9 (840.5)
383	881.9 (873.5)	849.5 (852.9)	847.2 (846.4)	827.6 (833.8)
393	874.5 (865.1)	843.1 (845.5)	839.7 (839.2)	822.0 (827.1)
403	866.7 (856.6)	836.3 (837.9)	831.9 (831.9)	816.4 (820.4)
413	858.4 (848.0)	828.5 (830.3)	823.7 (824.6)	810.5 (813.6)

^a The maximum error involved in ρ is $\pm 0.2\%$; the values in parentheses are the calculated densities which have an error of $\pm 1.5\%$.

The glass transition temperature was measured using Du Pont 990 DSC with a heating rate of 20 °C/min, using *n*-octane as the reference material; the results are summarized in Table X, which has an uncertainty of ± 2 K.

Results and Discussion

The analyses of the linear dependence of density on temperature (Figures 1–3) and the isothermal density–molecular weight and specific volume–molecular weight plots (Figures 4 and 5) of all the ester series reveal a significant dependence on the molecular weight and molecular structure. At a constant temperature and pressure, the liquid densities of the esters decrease with increasing molecular weight.

To elucidate the volume behavior further, the densities of these esters are compared with those of *n*-alkanes of similar molecular weight (API project 42 data) (11) at constant temperature (near 373 K) and pressure (Figure 4). Handbook data (12) on various liquids suggest that the densities of the liquids in a homologous series tend asymptotically toward a constant value (13). The isothermal liquid densities of *n*-alkanes increase asymptotically with successive addition of $-\text{CH}_2-$ groups, reaching a limiting value (14) of 0.8541. In methyl esters of fatty acids, this limiting value (15) is 0.8541.

While the concentrations of the end group CH_3 and the methylene group $-\text{CH}_2-$ were the same for both ester and alkane series, the observed trend of the densities of the ester liquids is clearly due to the influence of the average packing

Table V. Densities of 2-(Hydroxymethyl)-2-methyl-1,3-propanediol Trialkyl Esters

T/K	$\rho / (\text{kg m}^{-3})^a$							
	TMEP	TMEB	TMEV	TMEH	TMEO	TMEN	TMED	TMEPa
303	1038.6 (1040.3)	1003.6 (1009.8)	984.9 (987.3)	951.0 (956.2)	935.8 (945.1)	924.6 (935.9)		
313	1031.0 (1031.4)	996.0 (1001.8)	977.7 (979.8)	944.3 (949.5)	928.8 (938.6)	917.7 (929.6)		
323	1022.6 (1022.2)	988.1 (993.5)	970.0 (972.1)	937.2 (942.5)	922.4 (931.9)	911.2 (923.1)	906.2 (915.7)	
333	1013.8 (1012.7)	979.8 (984.9)	962.3 (964.1)	929.9 (935.3)	915.5 (924.9)	903.8 (916.3)	899.7 (909.2)	
343	1005.5 (1003.0)	971.8 (976.1)	954.5 (955.9)	922.8 (927.9)	908.8 (916.9)	899.1 (909.4)	893.2 (902.4)	869.5 (875.8)
353	997.0 (993.1)	963.3 (966.9)	946.5 (947.3)	915.4 (920.2)	903.0 (914.2)	890.2 (902.2)	886.3 (895.3)	863.4 (869.3)
363	989.7 (983.1)	957.1 (957.9)	937.0 (938.9)	908.4 (912.6)	894.7 (903.0)	883.0 (895.1)	879.5 (888.4)	857.1 (869.3)
373	980.8 (973.0)	946.6 (948.6)	928.0 (930.3)	901.0 (904.8)	888.0 (895.5)	875.5 (887.7)	872.7 (881.3)	850.7 (856.6)
383	971.3 (962.7)	939.2 (939.2)	920.6 (921.6)	894.1 (896.8)	881.5 (887.8)	867.8 (880.3)	865.7 (874.0)	844.4 (850.1)
393	962.6 (952.1)	932.6 (929.4)	913.1 (912.8)	887.0 (888.8)	874.8 (880.1)	861.4 (872.9)	858.7 (866.8)	838.1 (843.6)
403	954.4 (942.1)	923.2 (920.3)	905.8 (903.8)	879.7 (880.8)	868.0 (872.4)	854.2 (865.3)	852.1 (859.4)	831.5 (836.9)
413	945.9 (936.5)	915.4 (910.6)	910.7 (899.8)	872.2 (872.6)	861.0 (864.4)	848.6 (857.7)	845.2 (851.9)	824.6 (830.2)

^a The maximum error in ρ is $\pm 0.2\%$; the values in parentheses are the calculated densities which have an error of $\pm 1.5\%$.

Table VI. Densities of Pentaerythritol Tetraalkyl Esters

T/K	$\rho / (\text{kg m}^{-3})^a$							
	PETA	PETP	PETB	PETV	PETH	PETO	PETN	PETD
303			1046.5 (1050.6)	1013.6 (1023.6)	981.6 (986.2)	962.1 (972.8)	952.6 (961.6)	
313		1073.4 (1080.5)	1038.5 (1045.3)	1006.5 (1018.9)	975.0 (982.2)	955.7 (968.8)	946.1 (957.7)	
323		1065.2 (1071.6)	1030.4 (1037.3)	998.9 (1011.8)	967.9 (975.7)	948.7 (962.5)	939.0 (951.6)	932.7 (942.3)
333		1056.9 (1067.8)	1022.2 (1028.6)	991.3 (1003.5)	960.7 (968.2)	941.5 (955.3)	931.9 (944.6)	925.9 (935.5)
343		1048.9 (1056.7)	1013.8 (1019.1)	981.9 (994.6)	953.6 (960.2)	934.8 (947.7)	924.8 (937.2)	919.5 (928.3)
353		1040.3 (1040.5)	1005.6 (1009.1)	976.1 (985.3)	945.7 (951.8)	927.7 (939.5)	917.4 (930.2)	912.7 (920.6)
363	1077.8 (1072.0)	1032.0 (1029.7)	1000.1 (999.1)	968.5 (976.0)	928.4 (943.3)	920.6 (931.4)	910.3 (931.4)	906.1 (912.9)
373	1065.2 (1059.6)	1023.9 (1018.6)	988.9 (988.6)	961.2 (966.4)	921.4 (934.6)	913.7 (923.0)	903.2 (913.3)	896.4 (905.1)
383	1055.5 (1047.1)	1016.0 (1007.3)	978.1 (978.5)	954.4 (956.7)	914.6 (925.8)	907.2 (914.6)	895.5 (905.2)	889.9 (897.1)
393	1044.6 (1034.7)	1007.8 (996.1)	973.1 (968.2)	948.1 (947.0)	906.7 (917.1)	900.6 (906.2)	887.8 (897.0)	882.9 (889.1)
403	1033.7 (1022.0)	999.5 (979.8)	966.2 (957.7)	939.9 (937.0)	898.3 (908.2)	894.1 (897.6)	880.6 (888.7)	876.5 (881.4)
413	1022.4 (1009.3)	990.9 (973.3)	955.9 (947.2)	930.1 (927.3)	890.5 (899.2)	885.1 (888.9)	872.5 (880.5)	869.3 (873.0)

^a The maximum error in ρ is $\pm 0.2\%$; the values in parentheses are the calculated densities which have an error at $\pm 1.5\%$.

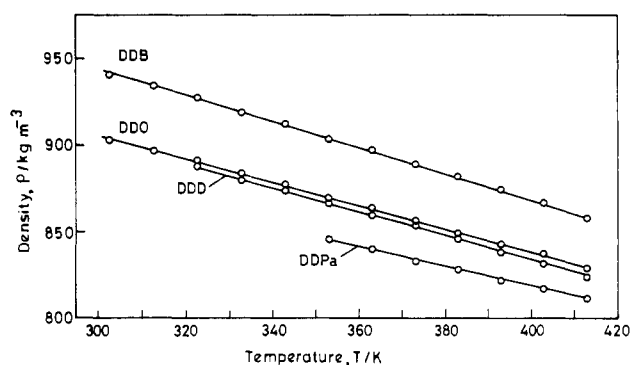


Figure 1. Variation of density ρ with temperature T for 1,10-decanediol dialkyl esters.

density and the concentration of $-\text{COO}-$ groups. It should be noted that the volume requirements for the rotation of a molecule must depend on its shape and the possible directional nature of its interaction with its neighbors. Since $\rho_{\text{CH}_2} \gg \rho_{\text{CH}_3}$, the increased densities in n -alkanes along the series are manifested by the successive addition of $-\text{CH}_2-$ groups. The observed decrease in the densities of the esters, with the successive addition of $-\text{CH}_2-$ groups, is due to the dilution of the $-\text{COO}-$ groups, since $\rho_{\text{COO}} \gg \rho_{\text{CH}_2}$.

It is evident from Figure 4 that the density follows the order

$$\text{PTEs} > \text{TTEs} \approx \text{TGEs} > \text{DSEs} \approx \text{DDEs} \quad (1)$$

We may explain this behavior on the basis of the relative degrees of compactness and steric interference to the free rotation. "Compactness" is a measure of the mean intramolecular distance between the component atoms of the molecule which is a function of the extent and relative proximity of the chain branching. In the n -alkane series, the absence of steric hindrance leads to an increase in free volume due to the free

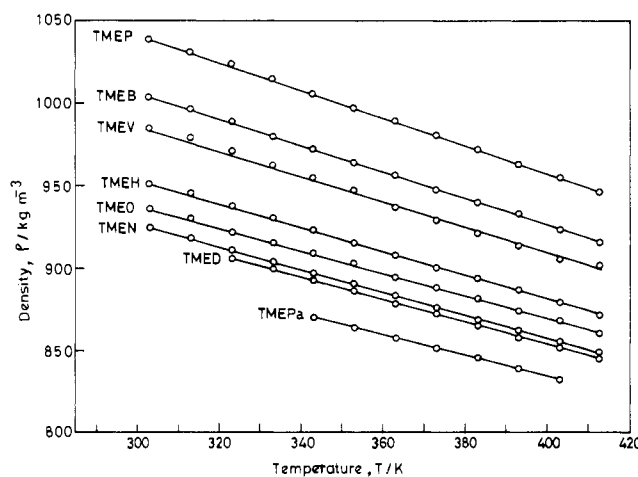


Figure 2. Variation of density ρ with temperature T for 2-(hydroxymethyl)-2-methyl-1,3-propanediol trialkyl esters.

rotation of the unhindered alkane chains (16). On the other hand, the presence of a large sterically hindered carbonyl group in the ester series would tend to reduce the degree of rotation and lead to a more closely knit arrangement of the molecules with greater intermolecular forces. This explains the behavior of n -alkanes as shown in Figure 4. Esters are denser than alkanes; the better packing in esters results in a decrease in specific volume; as the chain length in the ester series is increased by the successive addition of $-\text{CH}_2-$, it tends to loosen the closely packed arrangement of the molecules by disrupting the local configurational order of the $-\text{COO}-$ group. This results in an increase in the specific volume of esters with increasing $-\text{CH}_2-$ groups (Figure 5). Furthermore, as the molecular weight increases infinitely, the ester series tend toward a limiting value, like the n -alkanes, toward an asymptotic limit.

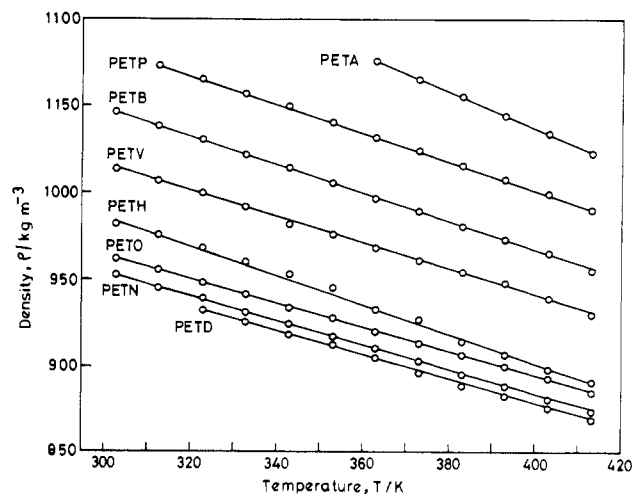


Figure 3. Variation of density ρ with temperature T for pentaerythritol tetraalkyl esters.

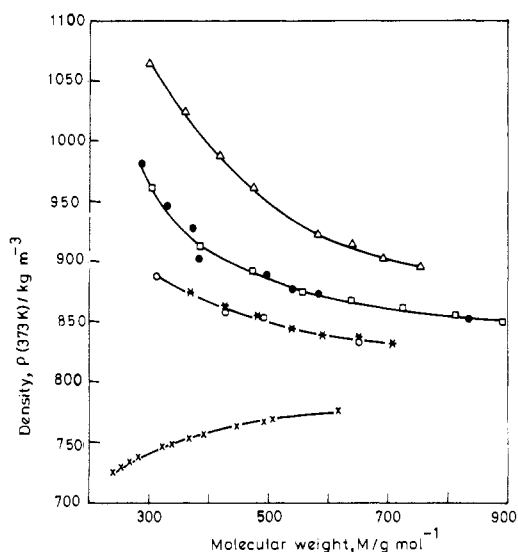


Figure 4. Variation of density ρ with molecular weight M : x, *n*-alkanes; *, DSEs; o, DDEs; □, TGEs; ●, TTEs; Δ, PTEs.

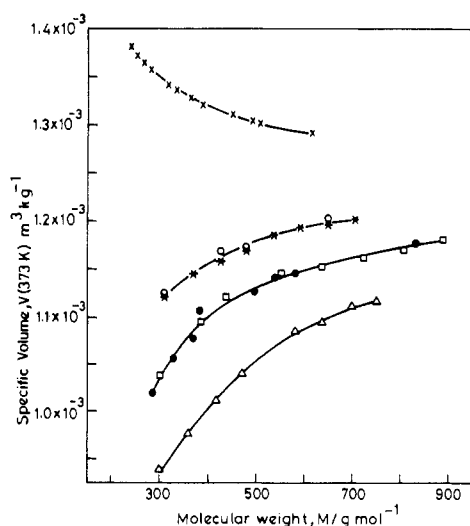


Figure 5. Variation of specific volume V with molecular weight M : x, *n*-alkanes; *, DSEs; o, DDEs; □, TGEs; ●, TTEs; Δ, PTEs.

To sum up, *n*-alkanes pack readily with parallel chain axes; this arrangement favors voluminous end to end contacts. In esters, on the other hand, there is a possible greater efficiency of packing for very small molecules than for the larger ones.

Table VII. λ and K Values of 1,10-Decanediol Dialkyl Esters^a

T/K	DDB	DDO	DDD	DDPa
303	0.1257	0.0926		
313	-1.5689	-2.31323		
323	0.1167	0.0861	0.0761	
333	-1.6829	-2.4796	-2.8779	
343	0.1123	0.0828	0.0732	
353	-1.7328	-2.5527	-2.9627	
363	0.1078	0.0795	0.0703	
373	-1.7787	-2.6200	-3.0407	
383	0.1033	0.0762	0.0673	0.0499
393	-1.8209	-2.6779	-3.1077	-4.3971
403	0.0989	0.0729	0.0644	0.0478
413	-1.8601	-2.7395	-3.1793	-4.4971
	0.0944	0.0696	0.0615	0.0456
	-1.8965	-2.7928	-3.2410	-4.5856
	0.0899	0.0663	0.0586	0.0435
	-1.9303	-2.8425	-3.2986	-4.6668
	0.0855	0.0630	0.0557	0.0413
	-1.9619	-2.8888	-3.2236	-4.7426
	0.0811	0.0597	0.0528	0.0392
	-1.9914	-2.9321	-3.4024	-4.8134
	0.0766	0.0565	0.0499	0.0369
	-2.0191	-2.9727	-3.4495	-4.8798

^a The upper value is $\lambda \times 10^{-3}$, and lower value is $K \times 10^3$.

A kinetic effect (17) also favors close packing in small ester molecules.

The density data have been empirically fitted (6) to the following equation:

$$\rho = \lambda + K\lambda^2 - 0.5281T + 1001.4 \quad (2)$$

where λ is a function of the absolute temperature (T), the number of carboxylic groups (N_{COO}), and the molecular weight (M) and K is a constant, which is a function of T , N_{COO} , and the number of methylene groups (N_{CH_2}). λ and K are defined as

$$\lambda = (B(T)N_{\text{COO}} + A(T))/M \quad (3)$$

and

$$K = \left[\frac{C(T)N_{\text{CH}_2} + D(T)}{E(T)N_{\text{COO}}} \right] \quad (4)$$

The functions $A(T)$, $B(T)$, $C(T)$, $D(T)$, and $E(T, N_{\text{COO}})$ are linear functions of T ; the latter is also a function of N_{COO} , N_{CH_2} , and M . The values of these functions were obtained as described in ref 6. The λ and K values are given in Tables VII-IX.

By using the empirical eq 2, densities have been calculated for all the ester series; the data are presented in Tables IV-VI. It is interesting to note that a change of structure such as branching does not produce any fluctuation in the density; the variations are generally within $\pm 1.5\%$. However, the densities show a rather strong and increasing dependence on the number of carboxylic groups, N_{COO} . Other properties of carboxylic esters, e.g., liquid heat capacity (18, 19) and entropy of fusion (20, 21), are also known to show similar effects.

Glass Transition Temperature. It is clear from the above discussion that density is strongly influenced by the molecular packing which arises due to the molecular rotation. It is well known that, at the glass transition temperature (T_g), the molecular rotation is restricted, and hence it should be related to the density. In *n*-alkanes, the density increases with molecular weight; interestingly, the T_g also gradually increases

Table VIII. λ and K Values of 2-(Hydroxymethyl)-2-methyl-1,3-propanediol Trialkyl Esters^a

T/K	TMEP	TMEB	TMEV	TMEH	TMEO	TMEN	TMED	TMEP _a
303	0.2342	0.2044	0.1813	0.1479	0.1354	0.1249		
	-0.6439	-0.8609	-1.0784	-1.5131	-1.7306	-1.9479		
313	0.2277	0.1988		0.1763	0.1438	0.1317	0.1214	
	-0.6253	-0.8364	-1.0474	-1.4694	-1.6804	-1.8914		
323	0.221	0.1931	0.1713	0.1397	0.1279	0.1179	0.1095	
	-0.6107	-0.8165	-1.0224	-1.4341	-1.6399	-1.8458	-2.0517	
333	0.2147	0.1874	0.1663	0.1356	0.1242	0.1145	0.1063	
	-0.5986	0.8002	-1.0018	-1.4051	-1.6067	-1.8083	-2.0099	
343	0.2082	0.1817	0.1612	0.1315	0.1204	0.1111	0.1031	0.0719
	-0.5884	-0.7865	-0.9846	-1.3808	-1.5788	-1.7769	-1.9749	-3.1634
353	0.2018	0.1761	0.1562	0.1274	0.1227	0.1076	0.0998	0.0694
	-0.5798	-0.7749	-0.9699	-1.3609	-1.5552	-1.7502	-1.9453	-3.1157
363	0.1953	0.1704	0.1512	0.1233	0.1129	0.1041	0.0966	0.0674
	-0.5724	-0.7649	-0.9574	-1.3423	-1.5348	-1.7272	-1.9197	-3.0745
373	0.1888	0.1647	0.1461	0.1192	0.1092	0.1007	0.0934	0.0652
	-0.5659	-0.7562	-0.9461	-1.3268	-1.5171	-1.7073	-1.8975	-3.0388
383	0.1823	0.1591	0.1411	0.1151	0.1054	0.0972	0.0902	0.0629
	-0.5603	-0.7485	-0.9367	-1.3133	-1.5015	-1.6897	-1.8779	-3.0074
393	0.1758	0.1534	0.1361	0.1110	0.1016	0.0937	0.0869	0.0607
	-0.5553	-0.7418	-0.9283	-1.3013	-1.4877	-1.6742	-1.8607	-2.9797
403	0.1693	0.1477	0.1315	0.1069	0.0979	0.0903	0.0838	0.0585
	-0.5509	0.7358	0.9207	-1.2906	-1.4755	-1.6604	-1.8453	-2.9549
413	0.1628	0.1421	0.1260	0.1028	0.0941	0.0868	0.0805	0.0562
	-0.5469	-0.7304	-0.9139	-1.2809	-1.4645	-1.6480	-1.8316	-2.9327

^a The upper value is $\lambda \times 10^{-3}$, and lower value is $K \times 10^3$.

Table IX. λ and K Values of Pentaerythritol Tetraalkyl Esters^a

T/K	PETA	PETP	PETB	PETV	PETH	PETO	PETN	PETD
303			0.2295	0.2022	0.1634	0.1491	0.1371	
			-0.3854	-0.4889	-0.6961	-0.7997	-0.9032	
313		0.2586	0.2238	0.1973	0.1594	0.1455	0.1338	
		-0.8364	-0.2911	-0.6393	-0.5256	-0.6038	-0.6819	
323		0.2521	0.2182	0.1923	0.1554	0.1418	0.1304	0.1207
		-0.1772	0.2422	-0.3072	-0.4373	-0.5023	-0.5674	-0.6324
333		0.2456	0.2126	0.1873	0.1514	0.1382	0.1271	0.1176
		-0.1549	-0.2116	-0.2684	-0.3820	-0.4388	-0.4956	-0.5524
343		0.2391	0.2069	0.1824	0.1474	0.1345	0.1237	0.1148
		-0.1395	-0.1907	-0.2419	-0.3442	-0.3953	-0.4465	-0.4976
353		0.2326	0.2013	0.1774	0.1434	0.1309	0.1203	0.1114
		-0.1284	-0.1755	-0.2225	-0.3166	-0.3637	-0.3431	-0.4578
363	0.2677	0.2261	0.1957	0.1725	0.1394	0.1272	0.1169	0.1083
	-0.0760	-0.1199	-0.1639	-0.2078	-0.2957	-0.3390	-0.3835	-0.4275
373	0.2601	0.2196	0.1901	0.1675	0.1354	0.1235	0.1136	0.1051
	-0.0718	-0.1133	-0.1548	-0.1963	-0.2792	-0.3207	-0.3622	-0.4036
383	0.2524	0.2131	0.1844	0.1626	0.1314	0.119	0.1102	0.1020
	-0.0683	-0.1079	-0.1474	-0.1869	-0.2659	-0.3054	-0.3449	-0.3844
393	0.2447	0.2066	0.1788	0.1576	0.1274	0.1162	0.1069	0.0989
	-0.0656	-0.1035	-0.1414	-0.1792	-0.2549	-0.2928	-0.3307	-0.3686
403	0.2370	0.1942	0.1732	0.1526	0.1233	0.1126	0.1035	0.0958
	-0.0633	-0.0998	-0.1363	-0.1792	-0.2458	-0.2823	-0.3188	-0.3686
413	0.2293	0.1936	0.1676	0.1477	0.1194	0.1089	0.1002	0.0927
	-0.0613	-0.0966	-0.1319	-0.1673	-0.2380	-0.2733	-0.2857	-0.3440

^a The upper value is $\lambda \times 10^{-3}$, and lower value is $K \times 10^3$.

with molecular weight (22) (Figure 6). The dependence of T_g on molecular weight in esters is rather perplexing (Table X). A pronounced but opposing trend is observed in linear and +-branched series; the Y-branched esters show an intermediate effect. Furthermore, this behavior seems to be more conspicuous after a molecular weight of 600, which we have shown as the limiting size for the segmental motion to occur (7).

Broadly, the variation of T_g can be considered separately for low molecular weight and high molecular weight compounds. In low molecular weight esters, we can say that there is a general decrease in T_g with molecular weight which is in consonance with the variation of density with molecular weight. In high molecular weight esters, the behavior of T_g with molecular weight seems to be very complex and the effect of structure is very glaring. In esters, a molecular weight of 600, irrespective of the branching, was taken as the approximate segment size for the flow process (7). This segment

size is strongly dependent on the nature of the liquid; for instance, in *n*-alkanes (23), the segment size is around 250. We have invoked the notion of a blob to explain the flow behavior in esters. In slightly concentrated polymer solutions, a single polymer chain could be visualized to consist of a succession of "blobs" (24) of certain diameter which act as hard spheres and are packed into a regular one-dimensional array. According to Benoit (24), the blob size in a slightly concentrated solution is approximately 50–100 Å. This size, however, in pure liquids would be much smaller. Following Flory's statistical approach (25, 26), the blob size was calculated for all the esters at their molecular weight of 600. For linear and Y- and +-branched esters, the blob size was found to be 11.2, 10.8, and 10.2 Å, respectively (9, 27). A diameter of about 11 Å could then be considered as the average blob size in these ester series.

As the molecular weight increases beyond 600, the branched segments start protruding out of the blob; however, they do

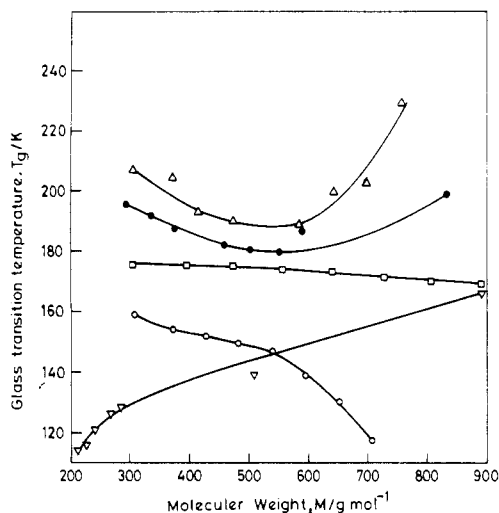


Figure 6. Variation of glass transition temperature T_g with molecular weight M : ∇ , n -alkanes; \circ , DSEs; \square , TGEs; \bullet , TTEs; \triangle , PTEs.

Table X. Glass Transition Temperatures (T_g) for Different Ester Series^a

linear ester	T_g /K	Y-branched ester	T_g /K	+ -branched ester	T_g /K
DBS	159	TB	176	PETA	207
DHS	153	TC	175	PETP	204
DOS	152	TO	175	PETB	192
DDS	148	TD	174	PETV	190
DDoS	146	TL	173	PETH	188
DTeS	138	TM	172	PETO	199
DHeS	130	TP	170	PETN	202
DOcS	117	TS	169	PETD	229
		TMEP	195		
		TMEB	192		
		TMEV	187		
		TMEH	182		
		TMEO	180		
		TMEN	179		
		TMED	188		
		TMEPa	198		

^a The error involved in T_g measurements is ± 2 K.

not interfere in the flow process as they tail out of the hole along with the blob. The tails protruding out of the blob cause some kind of hindrance or trammel, which is more effectively felt in +-branched compounds due to excessive branching. The T_g results clearly indicate that hindrance in +-branched compounds restricts the segmental motion, and hence T_g increases gradually with the increased obstruction in the segmental motion as the molecular weight increases. In linear series, not much hindrance is felt, and therefore the chain flexibility successively increases with molecular weight; as a result T_g decreases sharply. Another noticeable feature of T_g of linear esters is that T_g decreases rather sharply after

a molecular weight of 600. Due to the entanglement or hindrance, the linear chains may produce a large aggregation of entangled molecules, but unlike Y and + esters, these orientations will be linear in nature. Such long-chain orientation will favor the flexibility of the chain. The Y-branched esters, as expected, show an intermediate behavior between +-branched and linear esters.

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