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Structural Expressions of Long-Chain Esters on Their Plasticizing Behavior in Poly(vinyl chloride)

H. K. Shobha and K. Kishore*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

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ABSTRACT: This is the first comprehensive report on the influence of structure and molecular weight of long-chain esters on their plasticization behavior with PVC. Below a molecular weight of 550, there is a decrease in T_g with molecular weight in linear, three-branched and four-branched neat esters, which is explained by the dilution effect of carbonyl groups with an increase in chain length. In the high molecular weight esters above 550, T_g continuously decreases in linear esters, but in three-branched and four-branched esters it increases with the molecular weight, which is explained from the blob model. The dilution effect in the linear esters decreases the PVC–plasticizer interaction and consequently T_g increases with molecular weight both in the low and the high molecular weight esters. In the three-branched and four-branched esters the dilution effect is overtaken by structural effects. The carbonyl groups are shielded and less exposed to PVC in the beginning, but as the arms grow with molecular weight, they become more flexible which facilitates their interaction with PVC. This continuously decreases the T_g with molecular weight in three-branched and four-branched esters upto a molecular weight of 550, beyond which entanglement suppresses the flexibility and, as a result, T_g increases with molecular weight.

Introduction

Long-chain esters (molecular weight 300–2000), are commonly used as plasticizers in polymers due to their compatibility and permanence.[1] The plasticizers decrease the glass transition temperature of the substrate polymer and thus change its hard, glasslike properties to a soft and flexible state. Plasticizers are generally high-boiling liquids, which when added to polymers, reduce polymer–polymer interaction at the expense of polymer–plasticizer interactions and thus increase segmental mobility and polymer flexibility. The chain structure, molecular weight, and other related properties of the plasticizers provide sufficient indication of their compatibility and efficiency.[2–8] Thus, structure–property investigations would be rewarding for both the selection of plasticizers and the understanding of the plasticizing mechanism, which is very much lacking in the literature.

In the present investigation, we have studied the influence of branching and molecular weight of long-chain esters on their own glass transition behavior as well as their plasticizing ability in poly(vinyl chloride) (PVC). The branched liquids may also provide a good model for understanding the dynamics of branched polymers.[9] PVC is a very widely used polymer, but being hard and brittle it needs to be plasticized for most applications. The following homologous series of esters of varying molecular weight and structure were chosen: (i) dialkyl sebacate esters (DSEs) and 1,10-decanediol dialkyl esters (DDEs) which are linear, polar flexible molecules; (ii) triglycerides (TGEs) and trimethylolethane trialkyl esters (TTEs) which are three-branched, compact polar molecules; (iii) pentaerythritol tetraalkyl esters (PTEs) which are four-branched, polar, rigid and highly compact molecules.

The compatibility of plasticizers with PVC has been attributed to specific interactions involving the methine hydrogen of PVC and the carbonyl groups of the esters.[10–12] Hydrogen bonding involving the β-hydrogens of PVC and dipole–dipole interactions may also be present.[13] The polymer–plasticizer interaction can be evaluated by various methods, including studies of the diffusion of plasticizers in polymers.[14–26] Commonly the glass transition temperature (T_g) of polymers is measured,[27] which is lowered in the presence of plasticizers.

Experimental Section

Methyl acetate (MA), ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), isobutyl acetate (IBA), *sec*-butyl acetate (SBA), and *tert*-butyl acetate (TBA) were prepared by conventional procedures.[28] Various long-chain ester series used in the present investigation are listed in Tables I–III. The preparation of DSEs and TGEs is given elsewhere.[29] DDEs, TTEs, and PTEs were prepared by reacting 1,10-decanediol, trimethylolethane, and pentaerythritol with the appropriate acid chlorides in toluene using pyridine for removing HCl. The liquid esters were separated from the reaction mixture by fractional distillation and purified by vacuum distillation. Solids were purified by recrystallization.

The esters were characterized by IR and ^1H NMR spectroscopy. ^1H NMR spectra were recorded on a Varian T-60 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. The IR spectra were recorded using a Perkin-Elmer Model 715 IR spectrophotometer as neat liquids for the liquid samples and in Nujol for solid samples. All the esters were found to be pure within the sensitivity of these measurements.

The intrinsic viscosity $[\eta]$ measurements[30] of PVC solutions ranging in concentration from 0.35 to 0.46 g/dL in tetrahydrofuran (THF)/plasticizer (1:1 by volume) were determined using an Ubbelohde viscometer at 25 ± 0.1 °C.

Differential scanning calorimeter (DSC) measurements, on a Du Pont 990 DSC, were made to obtain the glass transition temperature (T_g). The heating rate employed was 20 °C/min with *n*-octane as a reference. Esters were added to PVC in 20 w/w %, and the T_g was measured with an error of around ±2 °C.

The inverse gas chromatographic (IGC) studies[31–35] were carried out on a Shimadzu gas chromatograph (Model GC-4C PF) equipped with a flame ionization detector. N_2 was used as the carrier gas. The column was prepared as follows. PVC was dissolved in THF and coated onto a Chromosorb-G support of 80/100 mesh, AW DMCS (Analab Inc.) by continuous stirring and slow evaporation of solvent at 60 °C under vacuum. The coated support was dried to constant weight and packed in stainless steel tubing. The amount of coated polymer was determined by combustion and ashing.[36] The esters were injected onto the PVC-coated column. The quantities measured were the retention time for the pulse of ester to pass through the column and the volume flow rate of the carrier gas. They were used to calculate the specific retention volumes (v_g°). The measurements were made at 90 °C, just above the T_g of PVC.

Densities were measured using a mercury-calibrated dilatometer.[37]

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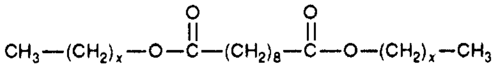
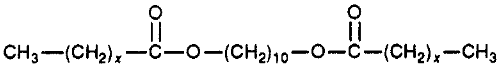
Table I
Structure and Molecular Weight of DSEs and DDEs



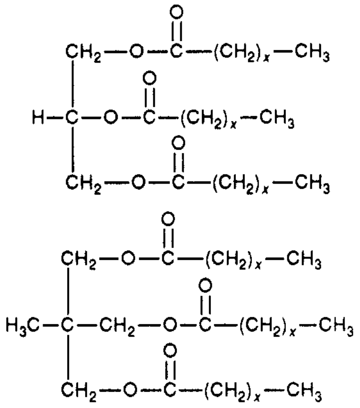
$$\mathrm{CH_3{-}(CH_2)_x{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_x{-}CH_3}$$



$$\mathrm{CH_3{-}(CH_2)_x{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_{10}{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_x{-}CH_3}$$

x	name	abbreviation	empirical formula	mol wt
3	di-*n*-butyl sebacate	DBS	$C_{18}H_{34}O_4$	314
5	di-*n*-hexyl sebacate	DHS	$C_{22}H_{42}O_4$	370
7	di-*n*-octyl sebacate	DOS	$C_{26}H_{30}O_4$	426
9	di-*n*-decyl sebacate	DDS	$C_{30}H_{58}O_4$	482
11	di-*n*-dodecyl sebacate	DDoS	$C_{34}H_{66}O_4$	539
13	di-*n*-tetradecyl sebacate	DTeS	$C_{38}H_{74}O_4$	595
15	di-*n*-hexadecyl sebacate	DHeS	$C_{42}H_{82}O_4$	651
17	di-*n*-octadecyl sebacate	DOcS	$C_{46}H_{90}O_4$	707
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	DDPa	$C_{42}H_{82}O_4$	650

Table II
Structure and Molecular Weight of TGEs and TTEs

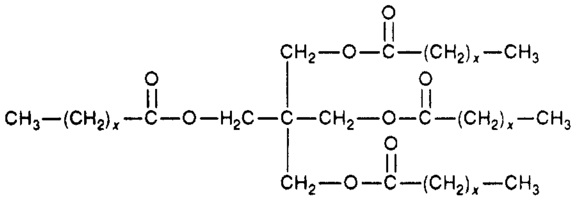


x	name	abbreviation	empirical formula	mol wt
2	tributyrin	TB	$C_{15}H_{26}O_6$	302
4	tricaproin	TC	$C_{21}H_{38}O_6$	386
6	trioctanoin	TO	$C_{27}H_{50}O_6$	470
8	tridecanoin	TD	$C_{33}H_{62}O_6$	554
10	trilaurin	TL	$C_{39}H_{74}O_6$	639
12	trimyristin	TM	$C_{45}H_{86}O_6$	723
14	tripalmitin	TP	$C_{51}H_{98}O_6$	807
16	tristearin	TS	$C_{57}H_{110}O_6$	890
1	trimethylolethane tripropionate	TMEP	$C_{14}H_{24}O_6$	288
2	trimethylolethane tributyrate	TMEB	$C_{17}H_{30}O_6$	330
3	trimethylolethane trivalerate	TMEV	$C_{20}H_{36}O_6$	372
5	trimethylolethane triheptanoate	TMEH	$C_{26}H_{48}O_6$	456
6	trimethylolethane trioctanoate	TMEO	$C_{29}H_{54}O_6$	498
7	trimethylolethane trinonanoate	TMEN	$C_{32}H_{60}O_6$	540
8	trimethylolethane tridecanoate	TMED	$C_{35}H_{66}O_6$	582
14	trimethylolethane tripalmitate	TMEPa	$C_{53}H_{102}O_6$	834

Results and Discussion

The T_g's of the plasticized PVC sample are given in Table IV; the T_g of neat PVC is 353 K. It is clear from Table IV that there is a decrease in T_g of the plasticized PVC, the extent of depression being directly related to the interaction of PVC with the plasticizer.[38] A satisfactory correlation between the efficiency of the plasticizer with the polymer–plasticizer compatibility and the polarity of the plasticizers is lacking in literature.[39] The difficulty stems from the fact that we do not have any method to evaluate the polarity of the plasticizers effectively; this significantly affects the polymer–plasticizer interaction energy. The compatibility, on the other hand, depends upon the energy of interaction and entropy of interaction between the polymer and the plasticizer. Any strong interaction between the polymer and plasticizer results in a negative entropy of mixing, which does not favor miscibility. For this reason, it is necessary to increase the combinatorial entropy of mixing which can be done only when the plasticizer molecules are very flexible. When other conditions are equal, the plasticizer molecules which possess sufficient internal mobility are always more compatible with the substrate polymer. The internal mobility here refers to the ability of the molecule to undergo conformational changes easily; it should be compatible with the polymer but need not dissolve completely in it. The compatibility limit should preserve the thermodynamic stability of the plasticized system over a wide range of temperatures encountered in processing, storage, and service.

Table III
Structure and Molecular Weight of PTEs



x	name	abbreviation	empirical formula	mol wt
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
Glass Transition Temperatures (T_g)[a] of Plasticized Poly (vinyl chloride)[b] Using Different Ester Series as Plasticizers

linear esters	T_g (K)	3-branched esters	T_g (K)	4-branched esters	T_g (K)
DDB	283	TMEP	297	PETA	309
DDO	288	TMEB	293	PETP	303
DDD	293	TMEV	293	PETB	302
DDPa	303	TMEH	293	PETV	300
		TMEO	289	PETH	298
		TMED	299	PETO	296
		TMEPa	308	PETD	303

[a] The error involved in the T_g measurement is ±2 K. [b] The glass transition temperature of PVC is 353 K.

One may note from Figure 1b that PVC–plasticizer miscibility is favored in linear compared to three-branched and four-branched esters. The ester groups having a high rotational barrier[40] (ca. 71 kJ mol^{-1}), make the four-branched esters, having four ester groups, the least flexible. Consequently, linear esters have the most and three-branched esters an intermediate flexibility. It is apparent

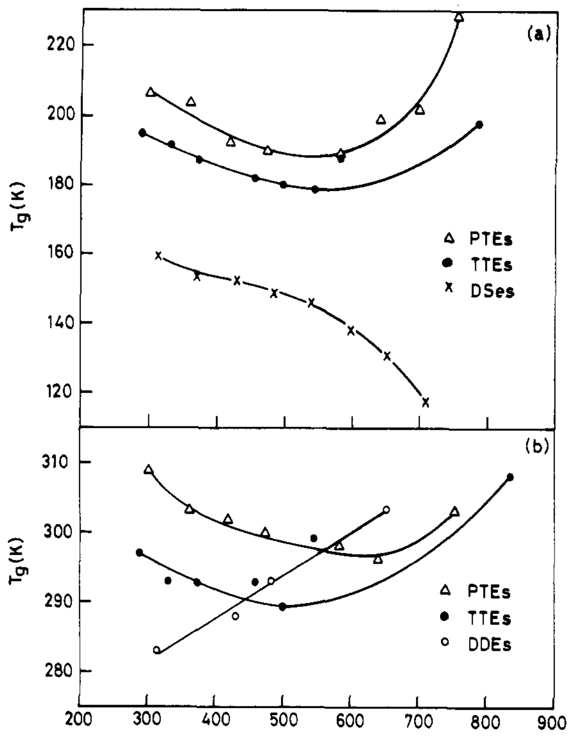


Figure 1. Variation of T_g with the molecular weight of (a) the neat plasticizers and (b) the plasticized PVC.

from Table IV that the plasticizing efficiency is broadly greater for linear esters compared to three-branched and four-branched esters. However, there are some discrepencies in the high molecular weight region (above 550), which will be discussed later. The glass transition behaviors of low molecular weight (below 550) esters and high molecular weight (above 550) esters are distinctly different (Figure 1). It would therefore be only logical to examine the effect of low molecular weight and high molecular weight esters separately for clarity.

Plasticizing Behavior of Low Molecular Weight (below 550) Esters. The polymer–plasticizer interaction parameter is qualitatively related to the dispersion and dipolar forces. Dipolar forces, being highly directional, are greatly affected by steric factors.[41] In linear esters, where there is no steric effect to counterfeit the dipolar forces, the T_g values increase with an increase in chain length. Due to the dilution of the ester groups, the plasticizer–PVC interaction decreases, resulting in an increase of T_g with chain length.

It would be interesting at this stage to look into the glass transition behavior of the neat plasticizers. A pronounced decrease in T_g with an increase in molecular weight is observed in linear esters, while in three-branched and four-branched series, T_g decreases initially and then increases. This behavior seems to be more conspicuous beyond a molecular weight of 550 ± 50, which is the limiting size[29] for segmental motion to occur. In low molecular weight compounds (below mol wt 550), there is a general decrease in T_g with molecular weight in all ester series. This is in agreement with the variation of density with molecular weight (Figure 2). The dilution effect reduces the interaction between carbonyl groups and brings about more flexibility as the chain length increases. The molecular weight dependence of T_g in high molecular weight compounds (above mol wt 550) seems to be very complex, and the effect of structure is very marked. The flow process in these high molecular weight esters has been modeled in terms of "blobs", where the flow occurs through a cooperative movement due to a process similar to somewhat loose entanglement.[42] This hindrance in these liquids, due to the tails protruding from the blobs, may be more effectively felt in four-branched compounds due to excessive branching. The T_g results clearly indicate that hindrance in four-branched compounds restricts the segmental motion as the molecular weight increases. In the linear series little hindrance is felt and therefore the chain flexibility successively increases with molecular weight; as a result T_g decreases sharply. The three-branched compounds understandably show an intermediate behavior between four-branched and linear compounds.

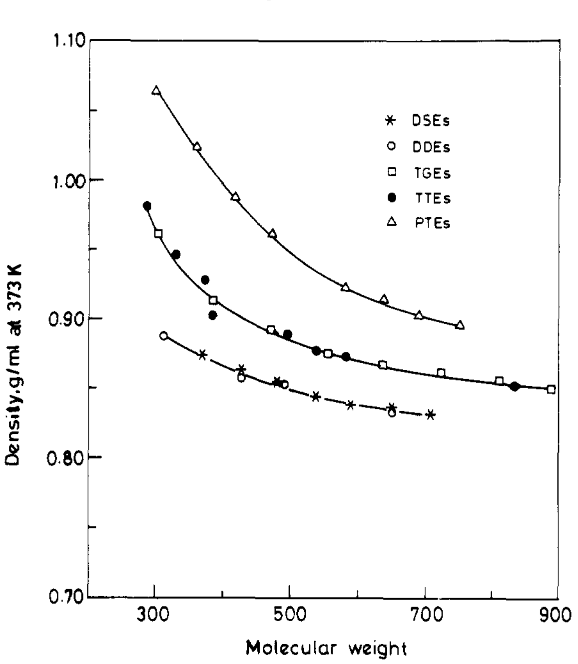


Figure 2. Variation of density with molecular weight.

Let us examine the behavior of plasticized PVC in light of the discussion on the glass transition behavior of neat esters. In three-branched and four-branched series, it may be noted that the T_g values of the plasticized PVC decrease with the increase in chain length—an effect which is opposite to that observed for the linear esters. By extending the same argument of the dilution effect in the three-branched and four-branched series, one should still observe an increase in T_g with an increase in molecular weight, although to a lesser extent, due to the dilution being distributed among three and four arms, respectively, in three-branched and four-branched esters compared to two arms in linear esters. Since we observe a decrease in T_g with the increase in molecular weight, the dilution effect is obviously being masked by stronger effects. In three-branched and four-branched esters, the carbonyl groups are shielded by the side chains and are less exposed to the PVC chains. As the chain length in esters is increased, the steric hindrance imposed by the branched arms is reduced; the arms pull apart to expose the carbonyl groups to facilitate the interaction with PVC. This effect prevails over the dilution effect resulting in a decrease in T_g with an increase in molecular weight. This is in accordance with the study made by Wurstlin and Klein,[43] where they concluded that the least efficient plasticizers are those molecules having the largest amount of steric hindrance. Jenckel and Heusch[44] also concluded from experimental measurements that the more elongated molecules are better plasticizers than the compact ones.

To further investigate the interaction of the chosen plasticizers with PVC, we have studied the PVC–plasticizer

Table V
Polymer–Solvent Interaction Parameter and Intrinsic Viscosity[a]

solvent	specific retention $\upsilon_g°$ (mL/g)	interaction param χ	intrinsic viscosity $[\eta]$	solubility param δ [(cal cm^{-3})$^{1/2}$]	interaction param χ
MA	4.90	1.30	1.09	9.36	0.01
EA	8.82	1.43	1.06	8.92	0.09
PA	16.01	1.50	1.03	8.73	0.16
BA	28.16	1.57	1.00	8.64	0.22
IBA	14.83	1.89	0.98	8.37	0.36
SBA	9.14	2.26	0.95	8.35	0.37
TBA	2.84	2.98	0.93	8.02	0.59

[a] The error in $\upsilon_g°$ is ±1.5%, in χ it is ±2.0%, and in $[\eta]$ it is ±1.5%.

interactions through the inverse gas chromatographic (IGC) method—a widely used technique for studying polymer–solvent interactions.[31–35] For this purpose, we need low-boiling esters as probes and PVC as the stationary phase. To simulate the structural effects of long-chain esters, we have selected low molecular weight model esters, varying in chain length and structures. For studying the effect of molecular weights, we have selected methyl, ethyl, *n*-propyl, and *n*-butyl acetates, and to study the effect of branching, we have selected esters having fixed molecular weights but varying in structure: *n*-butyl acetate for the linear esters, isobutyl and *sec*-butyl acetates for three-branched esters and *tert*-butyl acetates for the four-branched esters. Although these simple esters may not give exact representations of linear and branched esters, we hope they may provide a model of the linear, three-branched and four-branched esters.

The link between $\upsilon_g°$ and the polymer–solvent interaction parameter (χ) has been discussed in the literature.[45,46] The familiar Flory–Huggins approximation to polymer solutions leads to the following relationship when a high molecular weight ($\bar{M}_2$) polymeric solvent is involved.[45]

$$\chi = \ln\left[\frac{273.2R\upsilon_2}{\upsilon_g° V_1 P_1°}\right] - 1 - \frac{P_1°}{RT}(B_{11} - V_1) \qquad (1)$$

where V_1, $P_1°$, and B_{11} are respectively the molar volume, the vapor pressure, and the second virial coefficient of the pure solute at the temperature T (K); υ_2 and $\bar{M}_2$ are the specific volume and average molecular weight of the polymer, respectively. From $P_1°$ values[47–49] B_{11} values were calculated.[50] They are given in Table V which shows that it increases both with chain length and bulkiness. It is concluded that the interaction between PVC and ester decreases with an increase in the chain length and its bulkiness and follows the order

$$\text{MA} > \text{EA} > \text{PA} > \text{BA} > \text{IBA} > \text{SBA} > \text{TBA} \qquad (2)$$

Dilute solution viscosities have been used to assess the solvent power of liquids for a variety of polymers. Alfrey and Mark[51] have shown qualitatively that the intrinsic viscosity $[\eta]$, can be directly related to the thermodynamic affinity of a solvent toward the polymer. Liquids with high solvent power cause an expansion of the chain above the random coil dimensions and therefore increase the resistance toward flow. Hence $[\eta]$ values should be higher in good solvents. In low solvent power liquids, polymer chains remain in a tightly coiled state resulting in lower $[\eta]$ values. Hence, $[\eta]$ values (Table V) have been used to assess the polymer–solvent interaction.[51] The relative solvent power of the plasticizers, as indicated by their intrinsic viscosity, follows the sequence in eq 2. This trend shows that the interaction decreases with an increase in the chain length and its bulkiness. It may be mentioned here that the slopes of the reduced viscosity against concentration have also been used to assess the solvent power, but the interpretation is open to question. For instance, Frith[15] has shown that steeper slopes correspond to better solvents for PVC, whereas Spurlin[16] has shown the opposite to be true in cellulose derivatives.

In order to further substantiate the experimental results of the dilute solution viscosity and IGC, we have computed interaction parameter χ from the solubility parameter (δ) of the plasticizers and PVC. The following well-known approximate relationship has been employed:

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \qquad (3)$$

where V_1 is the molar volume of the ester and δ_1 and δ_2 are the solubility parameters of esters and PVC, respectively. We have calculated the solubility parameters by the method of additivity of group attraction constants, as proposed by Small.[52] The interaction parameters for the mixture of esters with PVC (Table V) show that the interaction decreases with an increase in chain length and bulkiness. The trend is found to be similar (eq 2) to that obtained from dilute solution viscosity and IGC measurements.

The results from both the above experimental methods suggest that as the chain length is increased, the interaction decreases. This is because lengthening of the aliphatic chain along the homologous series results in a dilution of the ester group which apparently weakens the PVC–ester interaction. Also the decrease in $[\eta]$ with an increase in the bulkiness in butyl acetate reduces the interaction between PVC and ester due to steric hindrance. This result is supported by the miscibility data of the aliphatic polyesters of short repeating unit with PVC[53] which shows that the interaction parameter χ of the blends increases by decreasing the number of aliphatic carbons in the polyester chain.

The concordance of the trend of interaction from all the above approaches in pleasing. It may be concluded that the PVC–model plasticizer interaction in linear esters decreases regularly with an increase in molecular weight as exhibited by the trend

$$\text{MA} > \text{EA} > \text{PA} > \text{BA} \qquad (4)$$

Furthermore, the PVC–plasticizer interaction in the so-called linear, three-branched, and four-branched model esters, at a fixed molecular weight, also decreases from linear to four-branched as exhibited by the trend

$$\text{BA} > \text{IBA} > \text{SBA} > \text{TBA} \qquad (5)$$

The above results on low molecular weight model esters are in agreement with the T_g behavior of the plasticized PVC with long-chain esters, as discussed earlier. To summarize, it may be emphasized that the polymer–plasticizer interaction intensity is the key factor in deciding the plasticization effect of these long-chain esters in PVC.

Plasticizing Behavior of High Molecular Weight (above 550) Esters. Let us first consider the linear esters. It may be seen from Figure 1 that the behavior of low molecular weight linear esters can be conveniently extended to high molecular weight esters, and therefore, the discussion offered for low molecular weight esters, namely the dilution effect, still prevails in the high molecular weight esters. However, the three-branched and four-branched esters both in their neat molecular environment and in the presence of PVC show an opposing trend.

In three-branched and four-branched esters, the T_g increases with molecular weight, in contrast to the decrease in T_g with the molecular weight in low molecular weight esters. We first analyze the attributes of the neat esters.

The increase in T_g with molecular weight signifies a decrease in flexibility with molecular weight. We have also said earlier that when the flexibility of the plasticizer diminishes, this results in the curtailment of the plasticizer–PVC interaction. One would therefore expect the T_g of the plasticized PVC to increase with a decrease in the flexibility. This is clearly reflected in the T_g trend of three-branched and four-branched series as a function of molecular weight. Although the reasons for the decrease in the flexibility of the neat high molecular weight long-chain esters with molecular weight cannot be exactly assigned, it is tempting to recall our discussion of the viscosity behavior of these long-chain esters at this stage. We have shown that above a molecular weight of 600, the flow behavior of the esters acquires some kind of segmental motion which has been adequately explained from the blob model. According to this model, the hindrance in the motion is maximum for the four-branched compared to the three-branched and linear series. It is perhaps this hindrance in high molecular weight esters that restricts the segmental mobility, and hence the T_g increases with molecular weight. It may be clearly stated here that the hindrance will be least in the linear esters and that that is why the dilution effect is so predominant in the linear esters that they exhibit a different trend than three-branched and four-branched series.

To conclude, we stress that the inherent structure of the plasticizer is of vital importance in deciding the polymer–plasticizer interaction and hence the plasticizing efficiency. T_g results clearly show that plasticizing efficiency would be high in linear esters below a molecular weight of 600 but above it three-branched esters would be preferred. The migration phenomena, as characterized by the flow behavior, are strongly dependent on branching and also on molecular weight. The three-branched esters will have an edge over the linear esters because of their higher activation barrier for viscous flow.[29] As far as the curtailment of volatile loss of plasticizers is concerned, the heat of vaporization is found to be independent of the structure and depends only on the molecular weight,[29] and so the high molecular weight esters may be preferred for this purpose.

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