Polymeric Structure in Some Molten Groups IIA and IIB Metal Dicarboxylates

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ABSTRACT: Groups IIA [i.e., Mg(2+), Ca(2+), and Ba(2+)] and IIB [i.e., Zn(2+), Cd(2+), and Pb(2+)] dicarboxylates were obtained by precipitation from aqueous solution. The salts were melted, quenched (when necessary), and characterized. Except for Pb(2+), the salts were highly viscous. The molten salts which were characterized by the presence of ionic carboxylates in their molecular structure exhibited polymeric structure resulting from a dynamic association equilibrium due to the ionic character of the metal ions. The ionic melts possessed relatively high melting temperatures and thermal stabilities, both of which have been found to be functions of the ionic character of the metal ions.

Introduction

Studies carried out on some divalent metal dicarboxylates showed that such salts display polymeric behavior in the molten state. This has been based particularly on the studies carried out on molten calcium sebacate ($Ca^{2+}Seb^{2-}$).[1-3] Molten calcium sebacate was described, through an approximation of the time-average molecular weight based on the rapid interchange of calcium sebacate with chain modifiers, such as $CaCl_2$, $Ca(OH)_2$, and NaCl, as being highly viscous and consisting of 10–15 associated repeat units:[4]

$$\underset{\text{salt}}{Ca^{2+}Seb^{2-}} \xrightarrow[t\,>\,325\ ^{\circ}C]{} \underset{\text{viscous melt}}{(CaSeb)_{10-15}} \xrightleftharpoons{\text{cooling}} \underset{\text{amorphous}}{(CaSeb)_n}$$

Little is known about the molecular structure and general behavior of similar molten salts of other dicarboxylic acids. There is the need, too, to look closely at the relationship between the behavior and properties of such molten salts and the periodic group of the divalent metals involved in their formation.

Experimental Section

Preparation. Mg(2+), Ca(2+), Ba(2+), Zn(2+), Cd(2+), and Pb(2+) dicarboxylates (i.e., suberate, sebacate, and dodecanedioate) were obtained by precipitation from aqueous solution. They were then melted (quenched when necessary) and characterized. Detailed information about the preparation will be provided elsewhere.[5]

Elemental Analysis. Carbon and hydrogen analyses were executed in the Micro-Analysis Laboratories of the Department of Inorganic and Structural Chemistry, University of Leeds.

Infrared Spectroscopy. The Perkin-Elmer 457 grating infrared spectrophotometer was used with KBr disks.

Thermal Properties. The melting temperatures and other thermal changes of the metal dicarboxylates were determined with the aid of a Reichert Thermovar (under crossed polars), a Du Pont 910 DSC, and a Du Pont 951 TGA.

Melt Viscosity. Melt viscosity measurements were carried out for the calcium (340 ± 1 °C), magnesium (330 ± 1 °C), cadmium (300 ± 1 °C), and lead (300 ± 1 °C) sebacates, due to temperature limitation, with a Contraves balance rheometer at the Contraves Rheology Laboratories, Zurich, Switzerland.

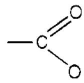
Isothermal and shear rate dependent viscosities were measured by using 5 g of dried salt specimen in a dried nitrogen atmosphere. Measurements were usually commenced 15 min after the salts were molten.

X-ray diffraction analysis was carried out as already reported.[6]

Results and Discussion

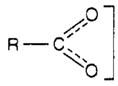
Elemental Analysis. The carbon and hydrogen analyses of the molten divalent metal dicarboxylates corresponded to the simple molecular structure $MOOC(CH_2)_nCOO$, where n = 6, 8, and 10 and M is the divalent metal.

Infrared Spectroscopy. The infrared spectra of the molten meta dicarboxylates are generally similar to those of the pure salt forms except that the absorption bands of the molten salts were broader and less defined. This is shown, for example, by the absorption spectra of cadmium dodecanedioate (Figure 1). The single carbonyl (C=O) absorption observed at 1640–1780 cm^{-1} for all the "parent" dicarboxylic acids (i.e., suberic, sebacic, and dodecanedioic) had disappeared on the formation of the metal dicarboxylates. Instead, it was replaced by two new bands at between 1350–1490 cm^{-1} and 1490–1690 cm^{-1}. These two bands correspond respectively with the symmetrical and antisymmetrical vibrations of the COO grouping.[7] The replacement of the single carbonyl band with two new ones was due to the ionization of the dicarboxylic acids, resulting in the equilibration of the two oxygen atoms attached to the carbon. The molten metal dicarboxylates are, in general, characterized by these two absorption spectra resulting from ionized carboxylate



The antisymmetrical COO-absorption band (1490–1690 cm^{-1}) is, however, very much more characteristic since many other vibrations may occur in the range 1300–1400 cm^{-1}.[8] In addition, the antisymmetrical COO vibration is the most intense of all the bands, which is an indication of the presence of ionic carboxylates.[7]

Previous studies[9] on the structure of some salts of phenylstearic acid showed, on the basis of the disappearance of the carbonyl frequency near 1700 cm^{-1}, the structure of a univalent metallic carboxylate salt to be



Generally, there is coincidence between the major spectra of the sodium and the molten divalent metal dicarboxylates. Except for the bands due to the C=O and in the intensities of all the bands generally, the spectra of the free acids are closely similar to those of the molten divalent metal salts. The C=O band was therefore taken

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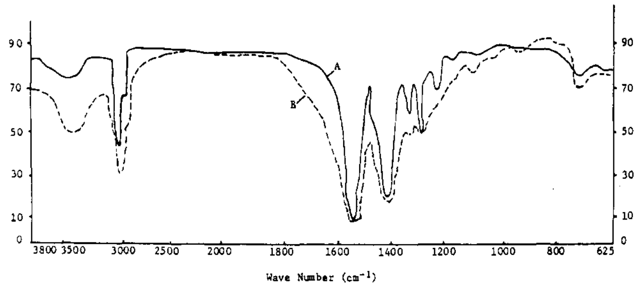


Figure 1. Absorption spectra of molten (B) and unmelted (A) cadmium deodecanedioate.

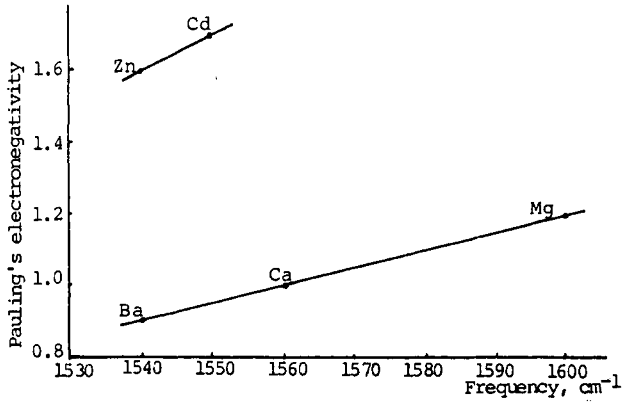
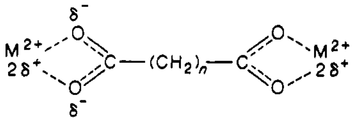


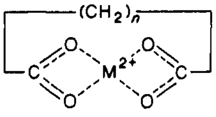
Figure 2. COO$^-$ antisymmetric stretching frequency versus Pauling's electronegativity of the metals.

as a basis for the structural description of the molten metal dicarboxylates. However, the slight difference between the C=O spectrum of one molten metal dicarboxylate and the other may be regarded as a factor related to some physicochemical properties of the metal.[10] For example, a plot of the antisymmetrical COO$^-$ stretching frequency of the molten salts of the groups IIA and IIB metals showed a linear relationship with Pauling's electronegativity of the metals (Figure 2).

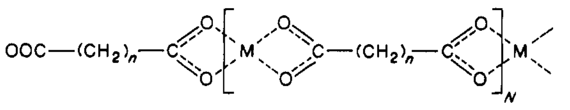
Since the infrared spectra of the molten divalent metal dicarboxylates are dominated by the absorption bands due to ionized carboxylate, the following molecular structure is proposed, whereby M^{2+} is the divalent metal and n = 6, 8, and 10.



The presence of a divalent metal in the molecular structure leads generally to strong polarity which could either result in (a) cyclic or (b) polycondensed linear molecular structure of the type



a



b

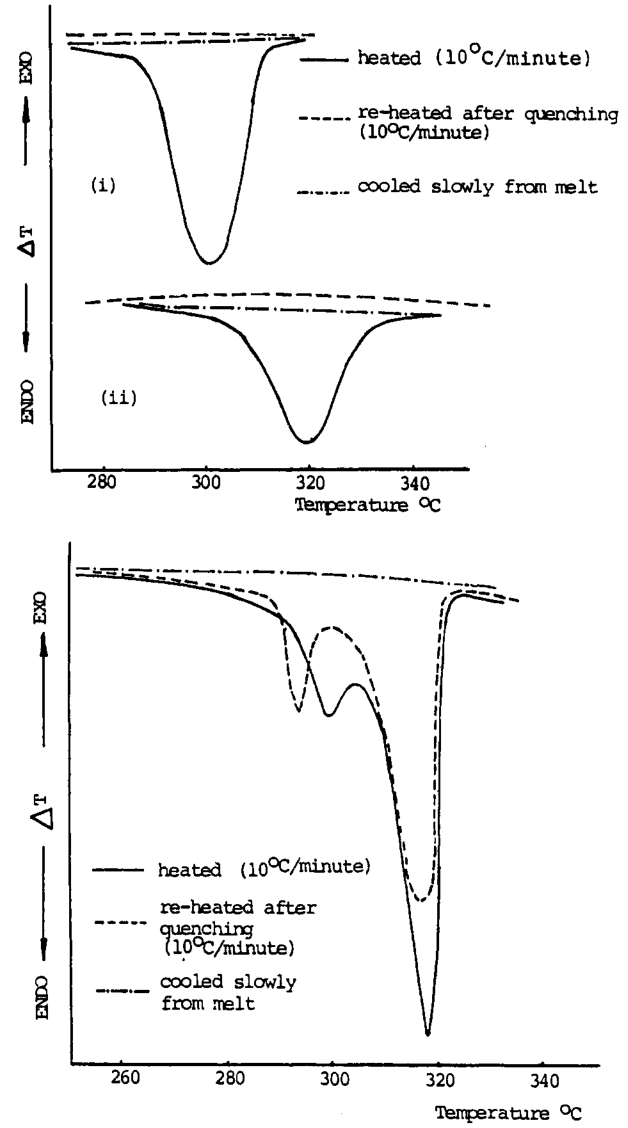
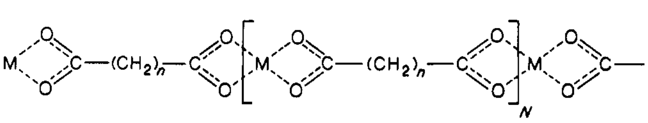


Figure 3. (a, Top) DSC curves of calcium dodecanedioate (i) and sebacate (ii). (b, Bottom) DSC curves of zinc dodecanedioate.

The association that takes place in the melt phase of the metal dicarboxylates may result from the ionic linkage of individual molecules or polymeric units or through ionic glasslike cross-links. The association through ionic links of individual molecules can lead to straight chain (c) or cross-link (d) formation where N, the number of associated units, is a factor of the ionic character of M, the divalent metal ion.



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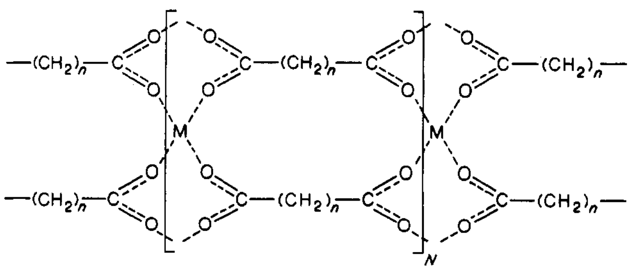


d

M = divalent metal ion
N = the number of associated units

Thermal Properties. The DSC analysis showed that the endotherms observed on melting of the Mg, Ca, and Ba dicarboxylates disappeared on quenching from the melt (Figure 3a), while Zn, Cd, and Pb showed reversible en-

Table I
Melting and Decomposition Temperature of the Divalent Metal Dicarboxylates in Relation to the Partial Ionic Character of the Divalent Metal Ions

M for $MOOC(CH_2)_nCOO$	ionic character, %	melting point (thermal stability)[a]		
		$n = 6$	$n = 8$	$n = 10$
Ba	82	(500)	410 (460)	375 (495)
Ca	79	370 (480)	330 (490)	290 (480)
Mg	73	332 (355)	325 (385)	279 (375)
Zn	59	(400)	(335–340)[b]	(298–318)[b]
Cd	55	(350)	(280–288)[b]	(270–275)[b]
Pb	51	(300–305)[b]	(275–280)[b]	(260–265)[b]

[a] Temperature at which 5% weight loss was recorded. [b] Recrystallization temperature; the temperature range at which some of the metal dicarboxylates recrystallized when quenched (liquid N_2) from the melt (T_m) and reheated (10 °C/min).

dotherms which were usually broader and less sharp (Figure 3b). Recrystallization did not take place during the quenchings in liquid nitrogen or on subsequent reheating of the Mg, Ca, and Ba dicarboxylates. The contrary was the case for the Zn, Cd, and Pb dicarboxylates which recrystallized when reheated (10 °C/min) after quenching in liquid nitrogen (Table I). There was no evidence for the presence of a region of specific heat increase during any of the reheats, so that no transition from amorphous glass to amorphous liquid (T_g) was observed. The failure of the Mg, Ca, and Ba salts to crystallize after melting is likely due to their greater tendency to form the three-dimensional network structures in the melt as opposed to the Zn and Cd salts which retain more linear structures that can partially recrystallize.

This type of melting behavior which resulted in the irreversible and reversible endotherms being replaced by broader peaks was most likely due to the formation of more amorphous products when the salts were melted. This explanation is supported by the results of the correlation crystallinity index.[6]

The melting temperatures of the metal dicarboxylates of a periodic group of the elements, e.g., the alkaline earth metals, showed some dependence on the partial ionic character. The higher the ionic character of the M–O bond of the cation of a group, the higher is the melting temperature (Table I). The melting temperatures of the metal dicarboxylates showed generally a decrease with an increase in the chain length of the dicarboxylic acid. Thermal gravimetric analysis revealed too that within the metals of the same periodic group the thermal stability is a function of the partial ionic character (Table I and Figure 4). The higher the partial ionic character the more thermally stable the metal dicarboxylate. For example, lead, which has the smallest ionic character (51%), is not only the least stable to heat but also the lowest melting. This implies that the relatively high ionic nature of the metal dicarboxylate bond leads to relatively good thermal stabilities. Decomposition results generally in the formation of inorganic compounds. For example, the plateau observed in the thermal gravimetric analysis curves of the lead dicarboxylates (Figure 5) at 58.8% (lead suberate), 54.8% (lead sebacate), and 51.3% (lead dodecanedioate) weight retention corresponds to the formation of PbO respectively at 460, 500, and 520 °C.

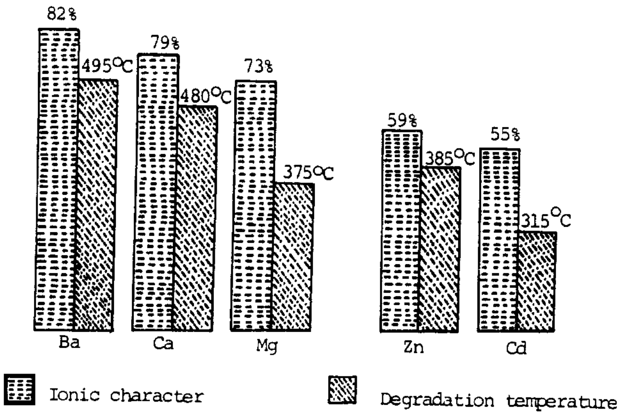


Figure 4. Diagram showing the partial ionic character and degradation temperature of the divalent metal dodecanedioates.

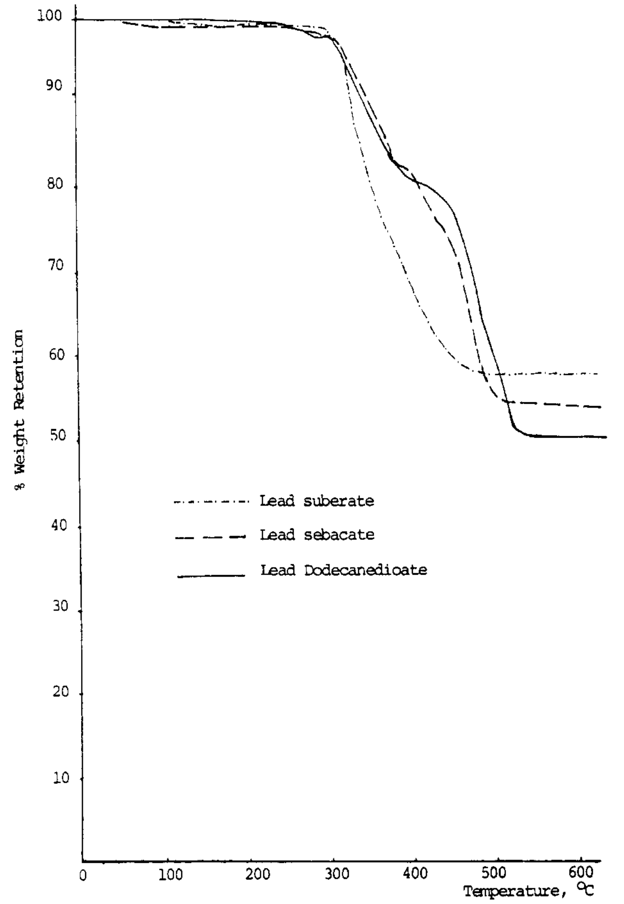


Figure 5. Thermal gravimetric analysis curves of lead dicarboxylates.

Rheological Properties. In general, the melts exhibit viscosities which vary with shear rate (Table II). A somewhat peculiar change in viscosities was observed for both the calcium and magnesium sebacate melts as the shear rate increased (Figure 6).

The melt viscosities of lead sebacate showed that the melt is nonpolymeric (Figure 6). The temperature (300

Table II
Rheological Properties: The Melt Viscosity of Some of the Divalent Metal Sebacates

sebacate	temp °C	melt viscosity (η, Pa s) at angular velocity, w s^{-1}				
		3.141	8.376	20.940	50.260	125.600
Cd	300	2.5	4.3	5.0	3.3	1.0
Mg	330	1.4×10^4	9.0×10^2	6.6×10^2	7.5×10^2	7.0×10^2
Ca	340	2.1×10^4	2.4×10^4	7.0×10	8.1×10	1.3×10^2
Pb	300	1.2	0.9	0.6	0.5	

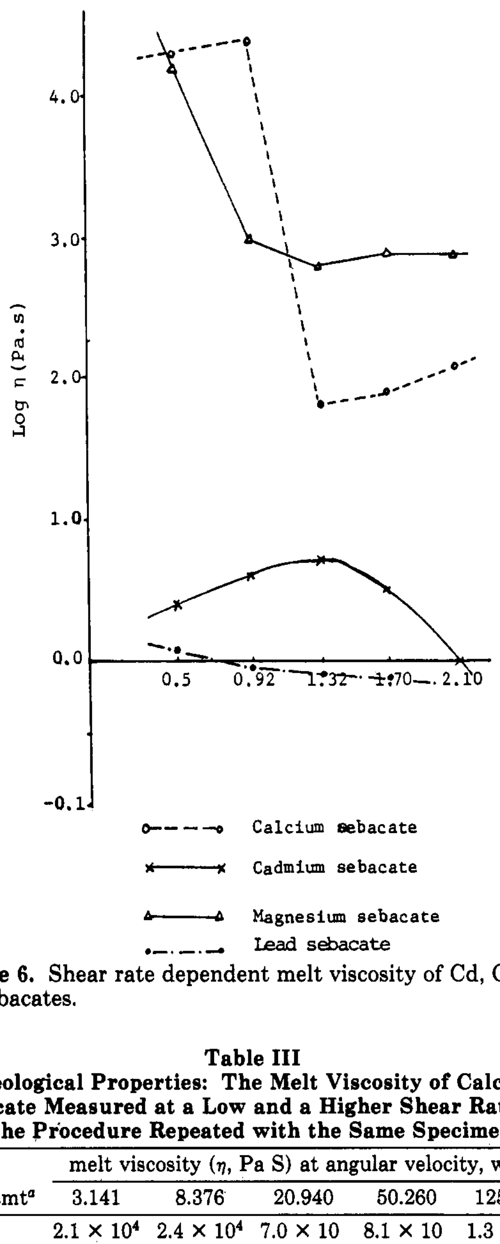


Figure 6. Shear rate dependent melt viscosity of Cd, Ca, and Mg sebacates.

Table III
Rheological Properties: The Melt Viscosity of Calcium Sebacate Measured at a Low and a Higher Shear Rate and the Procedure Repeated with the Same Specimen

	melt viscosity (η, Pa S) at angular velocity, w s^{-1}				
measmt[a]	3.141	8.376	20.940	50.260	125.600
I_1	2.1×10^4	2.4×10^4	7.0×10	8.1×10	1.3×10^2
R_1	2.6×10^4	2.0×10^4	8.0×10^2	7.4×10^2	3.9×10^2
I_2	1.9×10^4	2.0×10^4	7.8×10	7.8×10	1.0×10^2
R_2	2.2×10^4	1.9×10^4	7.0×10^2	7.2×10^2	1.9×10^2

[a] I = initial; R = repeat.

°C) at which the melt viscosity measurements were carried out was below the decomposition temperature, 330 °C (Table I), so that no degradation was observed.

The behavior of the cadmium sebacate melt was found to be more a function of change in chemical structure than shear rate dependence. This was shown by the infrared spectrum of the melt which was characterized by the presence of the ketone carbonyl absorption at 1700–1740 cm^{-1}. The zinc salts cannot be characterized here because of their high melting nature.

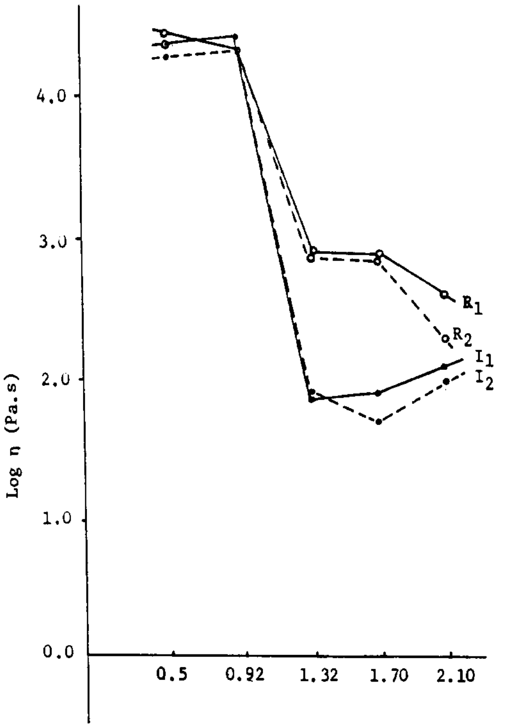
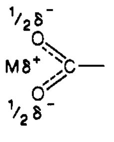


Figure 7. Shear rate dependent viscosities of calcium sebacate measured first at a low low and then a higher shear rate and the procedure repeated with the same specimen.

The peculiar nature of the melt viscosities of calcium sebacate was confirmed to be shear rate dependent (Table III and Figure 7) when the melt viscosity was measured at first from low to higher shear rate and then repeated. Since this peculiar behavior differs from those of the melts of conventional polymeric materials and because the unmolten salts did not exhibit any end group in their molecular structure, the high melt viscosities recorded for calcium and magnesium sebacates were taken as probable indications of association reactions taking place in the melt phases of the metal dicarboxylates. Since, according to Ubbelohde,[11] many features in molten salts depend on their polarizability, the high melt viscosities, i.e., the polymeric nature of these molten metal dicarboxylates, were regarded as resulting from the ionization of molecules due to polarization. As a result of polarization there is a single excess of charge, δ^+ and δ^-, along the metal carboxylate group



The polarization consequently leads to either intermolecular or interchain attraction. The intermolecular attraction results in long-chain formation while the interchain attraction leads to temporary cross-links which decrease the segmental mobility. The implication here is that ionization readily takes place in the molten magnesium and calcium salts which exhibit ionic character of 73% and 79%, respectively. On this basis, the assumption can be made that similar salts with ionic character (or electronegativity difference) of the metal–oxygen bond below a particular value may not exhibit a polymeric melt phase. This assumption is supported by the nonpolymeric nature of the melt viscosities of lead, which has an ionic character of 51%.

The molten salts exhibited some adhesive properties. They stuck to most surfaces—metals, wood, glass, ceramics, and concrete—just as they stuck such surfaces together. This hot-melt adhesive behavior, which is an area that requires further investigation, is likely to have had some influence on their rheological properties. The molten groups IIA and IIB salts were also spun into fibers. The fibers were, however, weak and brittle. In contrast, the lead salts could not be spun at all. This is very likely due to the nonpolymeric nature of the lead salts.

X-ray Diffraction Analysis. The correlation crystallinity index[6,12] showed generally that these viscoelastic molten salts are much more amorphous than their pure salt counterparts. The changes approximate to 50% reduction in crystallinity. This change in crystallinity could, according to Schultz[13] be due to cross-linking in the melt phase. Such cross-linking results in the melts becoming elastic and produces a reduction in crystallinity due to increased difficulty in chain orientation.

Conclusion

The groups IIA and IIB divalent metal dicarboxylates were obtained generally as highly viscous polymerlike materials in the molten state due to the ionic character of the metal ions. The polymeric behavior exhibited by these molten ionic metal dicarboxylates can be said to be a result of somewhat vague, dynamically shifting, unsatisfied associations first through the dicarboxylic acid chain and then between the metal dicarboxylate groups of neighboring chains. This type of association has, however, been shown to take place if the ionic character of the M–O bond of the cation is high enough. Molten lead (ionic character = 51%) dicarboxylates did not show any polymeric behavior.

The melts were thermoplastic when cooled from the melt and exhibited a relative degree of crystallinity almost as low as 50% of their pure (i.e., not melted) salt counterparts. The failure of the Mg, Ca, and Ba salts to crystallize after melting is a result of their greater tendency to form the three-dimensional network structures in the melt while the Zn and Cd salts tend to retain more linear structures which are able to partially recrystallize. In general the molten salts are characterized by high thermal stabilities ranging from 300 to 500 °C, which is a reflection of the highly ionic nature of these groups of materials. Except for lead, the molten salts which exhibit some hot-melt adhesive properties were spun into fibers which are weak and brittle.

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Registry No. $BaO_2C(CH_2)_6CO_2$, 84223-46-1; $BaO_2C(CH_2)_8CO_2$, 19856-32-7; $BaO_2C(CH_2)_{10}CO_2$, 117020-95-8; $CaO_2C(CH_2)_6CO_2$, 27796-71-0; $CaO_2C(CH_2)_8CO_2$, 19455-80-2; $CaO_2C(CH_2)_{10}CO_2$, 30687-91-3; $MgO_2C(CH_2)_6CO_2$, 85561-39-3; $MgO_2C(CH_2)_8CO_2$, 19922-46-4; $MgO_2C(CH_2)_{10}CO_2$, 99932-62-4; $ZnO_2C(CH_2)_6CO_2$, 85561-38-2; $ZnO_2C(CH_2)_8CO_2$, 19856-33-8; $ZnO_2C(CH_2)_{10}CO_2$, 55489-75-3; $CdO_2C(CH_2)_6CO_2$, 34284-36-1; $CdO_2C(CH_2)_8CO_2$, 4476-04-4; $CdO_2C(CH_2)_{10}CO_2$, 117020-96-9; $PbO_2C(CH_2)_6CO_2$, 85561-40-6; $PbO_2C(CH_2)_8CO_2$, 29473-77-6; $PbO_2C(CH_2)_{10}CO_2$, 117020-97-0.

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Notes

Solvent Partition Study in a Polymer Colloid Using Fluorescence Anisotropy Measurement

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Introduction

The fluorescence probe 1,6-diphenyl-1,3,5-hexatriene (DPH) has been extensively used to study order in lipid bilayers. The photophysical properties of DPH have been reviewed by Dale and Lakowicz.[1,2] The main advantage of DPH for these studies is the near colinearity of the absorption and emission dipoles and their alignment with the symmetry axis of the lipid bilayers. As a result, any change in the symmetry axis of the bilayer is easily detected.

A derivative of DPH with a cationic moiety affixed to the para position of one of the phenyl rings, 1-(4-(trimethylammonio)phenyl)-6-phenyl-1,3,5-hexatriene (TMA-DPH), was prepared by Prendergast et al.[3] The cationic moiety tethers the molecule at the lipid–water interface and the DPH part of the molecule is intercalated with the lipid.[3-5] The photophysics of TMA-DPH in the lipid bilayer was found to be similar to that of DPH.[3,6] TMA-DPH has extremely low solubility in water and its fluorescence activity in water alone is too low to be observable.[3,7]

In our studies, TMA-DPH was employed to examine changes in the local environment of the polymer colloid particles upon solvent addition. As in the case of lipid bilayers, it is assumed that the cationic end of the TMA-DPH molecule is located at the water–polymer interface and DPH part of the molecule is positioned among the polymer chains inside the polymer particle. Therefore, the anisotropy results reported here correspond to the local environment accessible to the probe molecule, which is estimated to be approximately 20–40 Å from the surface of the colloid particle.

The solvent added to the polymer colloid partitions between the aqueous and the polymer phases. The solvent partitioning into the polymer phase increases the mobility of the probe due to plasticization of the polymer. This change in the local environment is measured as a change in the fluorescence anisotropy of the TMA-DPH.

Experimental Section

The polymer colloid used for this study is a dialyzed colloid