

Figure 3. The plot of $\ln K$ vs. $(D-1)/(2D+1) \times 10$ for NDMPI at 25°C .

listed in Table 5 by use of eqs. (7), (8), and (9) to result in Table 7. The large negative values of $\Delta H^\circ_{\text{a}}$ and $\Delta S^\circ_{\text{a}}$ proved that the water molecules became more ordered around the NDMPI ions by their hydration.

Thermodynamic properties evaluated from eqs. (11), (12), and (13) were tabulated in Table 8. The fact that ΔS° values are positive means the formation of NDMPI ion goes with dehydration. The ΔS° values increased as the water content ascended, which proved that the equilibrium of eq. (1) is controlled by entropy when water content rises.

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Synthesis and Properties of Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer (VI). Homologous Series of α, ω -Bis [4-(*p*-substituted benzyloxy)benzyloxy]alkanes*

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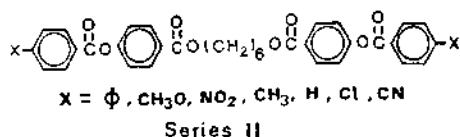
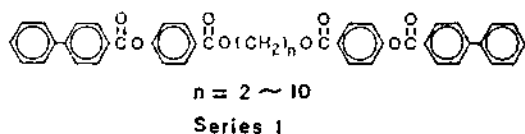
The thermal and optical properties of two new series of thermotropic, liquid crystalline compounds were studied by differential scanning calorimetry and on the hot-stage of a polarizing microscope. The first series contained two identical mesogenic units, 4-(*p*-phenylbenzyloxy) benzoate moieties, at both ends of the polymethylene spacer of varying lengths and the second series, mesogenic units with different substituents and the hexamethylene group as the central spacer. A thermodynamic analysis of the phase transitions of the compounds was made and the results were discussed in relation to their chemical structures.

Introduction

The mesomorphic properties of several different series of main chain polyesters recently were reported by us. These polymers contained mesogenic units of dyad or triad aromatic esters interconnected through flexible spacers such as polymethylene, polyoxyethylene or disiloxyl groups¹⁻⁵. We also reported that the thermotropic behavior of compounds which have two terminal mesogenic units and a central spacer is very similar to that of main chain polymers consisting of the same mesogens and spacers⁶⁻⁸.

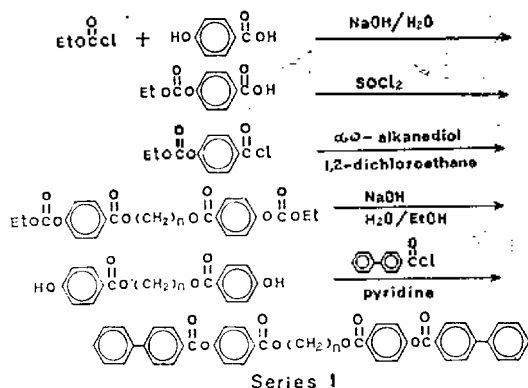
As a part of our continuing efforts to learn more about the relationship between structural feature and liquid crystalline properties, we have prepared two different series of compounds, I and II. The compounds of the Series I have two terminal mesogenic units based on 4-(*p*-phenylbenzoyloxy) benzoate ester bracketing a central polymethylene spacer of varying length, while those of the Series II consist of mesogens with various substituents and the hexamethylene spacer. Since it is well known that the phenyl group is capable of strongly stabilizing mesophases of the parent compounds, this substituent was chosen for the compounds of Series I^{6,9,11}.

Their phase transitions and thermotropic behavior were investigated by differential scanning calorimetry (DSC) and on the hot stage of a polarizing microscope.



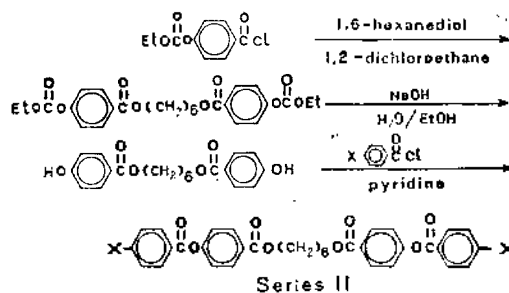
Experimental

Synthesis of the Compounds. The compounds were prepared by the following route;



Scheme 1. Synthesis of the Compounds of Series I.

*For the number 5 of this series refer to J.-I. Jin and J.-H. Park, *Mol. Cryst. Liq. Cryst.*, **110**, 293 (1984).



Scheme 2. Synthesis of the Compounds of Series II.

The aromatic diols, α,ω -bis(*p*-hydroxybenzoyloxy) alkanes were prepared following the method described in the literature^{3,12}. The final compounds, α,ω -bis[4-(*p*-substituted benzoyloxy) benzoyloxy] alkanes, were synthesized by reacting *p*-substituted benzoyl chlorides (0.02 mole) with the aromatic diol (0.005 mole) which was dissolved in 30ml of dry pyridine. The reaction mixture was stirred under a nitrogen atmosphere for 5 hours at room temperature and then at 70°C for 2 hours. At the end of the reaction the mixture was poured into cold water with vigorous stirring. The precipitates were washed with 0.1N aqueous NaOH and then again with distilled water. The crude products were recrystallized from various solvents. The yields and recrystallization solvents are tabulated in Table 1 and 2. Structures of the compounds were confirmed by elemental analysis and IR (Perkin-Elmer Infrared Spectrometer 710B) and NMR (Varian Associates EM 360A) spectra of the compounds. *Study of Thermal and Optical Properties of the Compounds.* Thermal transitions of the compounds were studied under a nitrogen atmosphere by DSC (Du Pont 910). Heating and cooling rates were constantly maintained at 10°C/min. Indium was employed as a standard for calibration. Optical textures of the mesophase and thermal transitions of the compounds were also examined on the hot-stage (Mettler, FP-52) attached to a polarizing microscope (Leitz, Ortholux).

Results and Discussion

Properties of the Compounds of Series I. For the compounds of this series, one terminal mesogenic unit, 4-(*p*-phenylbenzoyloxy) benzoyl, was used, while the length of polymethylene spacer was varied. These compounds can be divided into two different groups according to their thermal phase transition behavior. The compounds having polymethylene spacer with $n=2, 3, 7, 9$ and 10 exhibit only one endothermic peak on the heating run of DSC analysis, but two exothermic peaks on the cooling cycle. This observation together with microscopic examination lead us to the conclusion that these compounds were monotropic and underwent a direct solid→isotropic liquid transition upon melting, but two phase transitions on the cooling cycle from isotropic liquid to solid through a liquid crystal phase. The compound with $n = 7$ also showed two exothermic peaks on the DSC cooling cycle thermogram. However, the peak appearing at the higher temperature corresponds to the transition from the isotropic liquid phase to a liquid crystal phase and the

TABLE 1: Yields and Recrystallization Solvents of Series I Compounds

Methylene no. n	2	3	4	5	6	7	8	9	10
Yield, wt. %	93	87	96	85	96	80	92	84	87
Recryst. Solv.	Toluene Butanol	Toluene Butanol	Toluene	Ethanol Butanol	Toluene DMSO	Butanol	Toluene Butanol	Butanol Acetone	Toluene

TABLE 2: Yields and Recrystallization Solvents of Series II Compounds

Substituents x	ϕ	NO_2	CH_3O	CH_3	H	Cl	CN
Yield, wt. %	96	97	94	98	92	96	94
Recryst. Solv.	Toluene DMSO	Toluene	Butanol	Butanol	Butanol	Butanol	Butanol

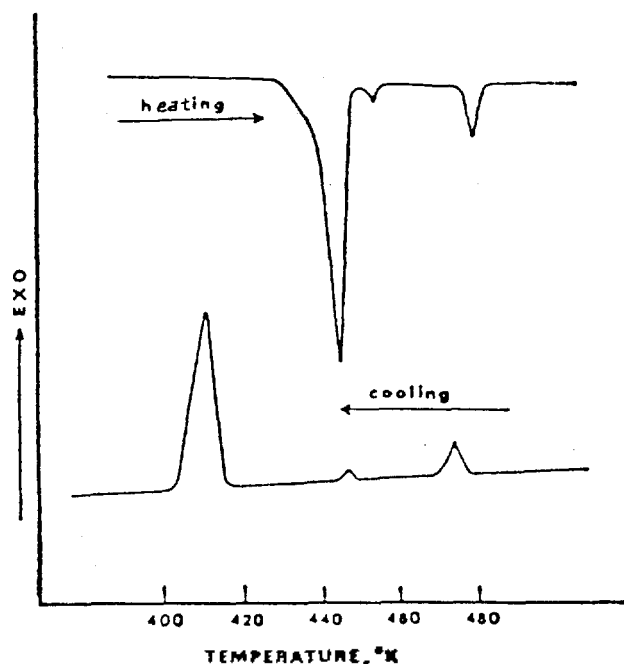


Figure 1. DSC thermogram of the Series I Compound with $n = 6$. Heating and cooling rates were $10^\circ\text{C}/\text{min}$.

one at the lower temperature to the phase transition from a liquid crystal phase to another liquid crystal phase. No crystallization peak was observed until the sample was cooled to 0°C . Such a phenomenon was confirmed by visual observation on the hot-stage of a polarizing microscope.

The compounds of the polymethylene spacer with $n=4$, 5, 6 and 8 belonged to the second group, enantiotropic liquid crystalline compounds exhibiting the formation of mesophases both on heating and cooling. The $n=4$ compound formed only one mesophase on heating. However, on cooling it exhibited a three step phase transition from isotropic liquid phase to solid through two different mesophases. On the contrary, the compounds with $n=5$ and 8 exhibited two phase transitions, both on heating and cooling, indicating that only one mesophase was formed. The compound with $n=6$, however, was unique in that both in its heating and cooling cycles DSC thermograms show three peaks reflecting the formation of two different mesophases (see Figure 1).

Throughout the DSC analysis of the compounds it was

repeatedly observed that the degree of supercooling for the transitions from the isotropic melts to the mesophases was far less than that for the transitions from the mesophases to crystalline solids. The same phenomenon has often been observed for other liquid crystalline compounds and polymers^{2,3}.

The phase transitions hypothesized from the results of DSC analysis were consistent with polarizing microscope observations. Optical textures observed for each compound were tabulated in Table 3. The $n=4$ compound shows a Schlieren optical texture upon melting, characteristic of the nematic mesophase. However, on cooling it formed the threaded optical texture, characteristic of the nematic mesophase at the higher temperature range. The smectic phase, judging by its fan-shape, most probably smectic A phase, was formed at the lower temperature range (see Figure 2 and 3). In the case of the $n=5$ compound, surprisingly enough, only the smectic A phase appeared on cooling the isotropic liquid, while the nematic phase was the only mesophase observed on melting the solid sample. The other enantiotropic compounds showed the same optical textures both on heating and cooling, see Table 3. The observations made on the microscope suggest that, as the alkyl group attached to a mesogenic group become longer, the compounds tend to form a smectic phase. It is believed that long spacers allow the mesogenic units to form an ordered lamellar structure giving rise to the smectic mesophases. Similar tendencies were reported earlier by others for other types of compounds^{6,7}.

The thermodynamic data for the phase transitions are listed in Table 3. The positions of peak maxima in DSC thermograms were taken as the transition temperatures. Heating curves were used for the determination of melting points of the compounds. However, the cooling curves were used to analyze the transition temperatures from isotropic to mesophases (T_i) and those from the mesophases to solid (T_c) because many compounds were found to be monotropic. The melting transition temperatures, T_m , and transition temperatures from the isotropic to mesophases, T_i , of the compounds decreased regularly in a zig-zag fashion as the length of the spacer, n , increased (see Figure 4). Both T_m and T_i for the compounds with an even number of methylene units were higher than their neighbors with odd n 's. Similar trends were

TABLE 3: Thermal Properties and Thermodynamic Data for the Phase Transitions of Series I Compounds^a

n	L.C. Props. ^b	Optical Texture ^c	$T_m, ^\circ\text{C}$	$T_i, ^\circ\text{C}$	$T_c, ^\circ\text{C}$	$\Delta T, ^\circ\text{C}$	ΔH_i KJ/mole	ΔH_c KJ/mole	ΔS_i joule/mole ^o K	ΔS_c joule/mol ^o K	$\frac{\Delta H_i}{\Delta H_c}$ %
2	Mo	N	252.3	217.8	211.0	6.8	2.27	26.0	4.62	53.8	8.72
3	Mo	N	206.0	146.3	112.1	34.2	1.21	10.8	2.87	28.0	11.1
4	En	N	231.8	232.5	186.2	46.3	4.02	50.2	7.95	109	8.01
		S		210.5		22.0	3.93		8.14		7.82
5	En	(N) ^d	133.2	(144.2) ^d	—	—	(2.25) ^d	—	(5.40) ^d	—	(8.34) ^d
		S		132.8			2.83		6.98		—
6	En	N	171.8	203.8	139.9	63.9	3.86	33.6	8.09	81.3	11.5
		S		178.7		38.8	1.11		2.45		3.31
7	Mo	N	126.1	105.2	—	—	1.63		4.31	—	—
		S		74.5			0.32		0.93		—
8	En	S	169.8	187.5	112.3	75.2	1.81	23.2	3.93	60.1	7.82
9	Mo	S	126.3	109.8	83.2	26.6	0.51	28.9	1.32	81.2	1.76
10	Mo	S	154.9	145.4	115.0	30.4	3.40	40.4	8.11	104	8.40

^aExcept T_m values, all the data were obtained from DSC cooling curves. ^bMo and En respectively designate monotropic and enantiotropic formation of liquid crystal phases. ^cN and S respectively stand for nematic and smectic phases. ^dValues shown in the parentheses are those obtained from the heating curves of DSC thermogram.

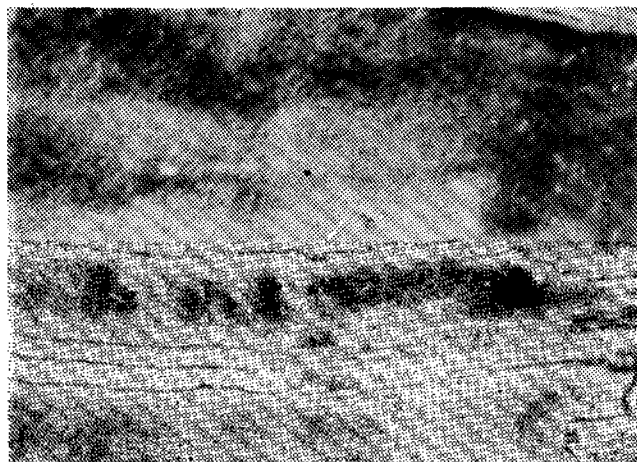


Figure 2. Photomicrograph of the Series I compound with $n = 4$ taken at 232°C (magnification; 300 x) on heating cycle.

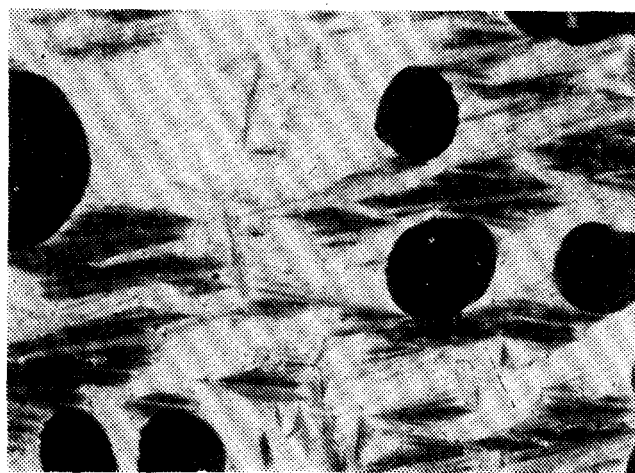


Figure 3. Photomicrograph of the Series I compound with $n = 4$ taken at 206°C (magnification; 300 x) on cooling cycle.

reported for many other series of low molecular liquid crystal compounds⁶ and also for semiflexible thermotropic polymers³. These trends suggest that spacers with even n 's favor more efficient packing and better alignment of the molecules in solid as well as in liquid crystal phases¹³.

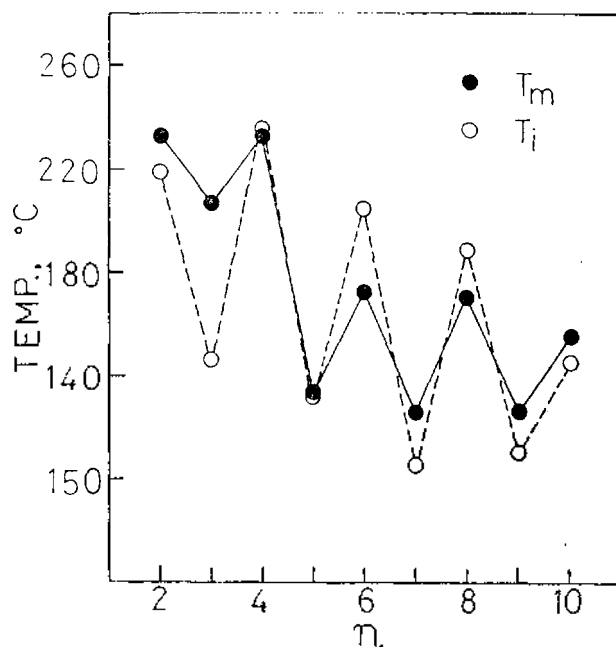


Figure 4. Dependence of the melting temperatures (T_m) and transition temperatures (T_i) from isotropic to mesophases of the Series I compounds on the length of the central polymethylene, n . T_m 's were obtained from the heating curves of DSC thermogram while T_i 's were from the cooling curves. Heating and cooling rates were $10^\circ\text{C}/\text{min}$.

Table 3 shows that the values of the enthalpy change for isotropic-to-mesophase transitions, ΔH_i , ranged from about 8 to 16 % of those of melting, ΔH_m , in magnitude, which is very high when compared with the corresponding values of similar compounds having only one mesogenic unit¹⁴. Another interesting point observed was that the ΔH_i values for the compounds with an even number of methylene units were generally significantly higher than those for the odd-number compounds. The ΔH_i value for the compound with $n=9$ was particularly lower than those for the other members of this series. The reason for this is not yet clear.

The values of ΔS_i for compounds with even-numbered

TABLE 4: Thermal Properties and Thermodynamic Data for the Phase Transition of Series II Compounds^a

Subst.	L.C	Optical	$T_m, ^\circ\text{C}$	$T_i, ^\circ\text{C}$	$T_c, ^\circ\text{C}$	ΔH_m	ΔH_i	ΔH_c	ΔS_i	ΔS_c	$\frac{\Delta H_i}{\Delta H_c}$
X	Props. ^b	Texture ^c				KJ/mole	KJ/mole	KJ/mole	joule/ mole ^o K	joule/ mole ^o K	%
ϕ	En	N	171.8	203.8	139.9	34.0	3.86	33.6	8.09	81.3	11.5
		S		178.7			1.11		2.45		3.31
CH ₃ O	Mo	N	150.0	138.8	63.9	54.6	3.61	36.0	8.77	107	10.0
NO ₂	Mo	N	153.9	131.3	107.6	57.0	4.97	49.9	12.4	131	9.96
CH ₃	Mo	N	142.7	101.3	98.9	58.2	3.84	53.8	10.3	145	7.16
H ^d	—	—	157.4	—	—	73.6	—	—	—	—	—
Cl ^d	—	—	162.4	—	—	67.2	—	—	—	—	—
CN ^d	—	—	202.4	—	—	57.9	—	—	—	—	—

^aExcept the values of T_m and ΔH_m , all the data were obtained from the cooling curves of DSC analysis. ^bEn and Mo respectively designate monotropic and enantiotropic formation of liquid crystal phases. ^cN and S respectively stand for nematic and smectic phases. ^dThese compounds did not form a liquid crystal phase.

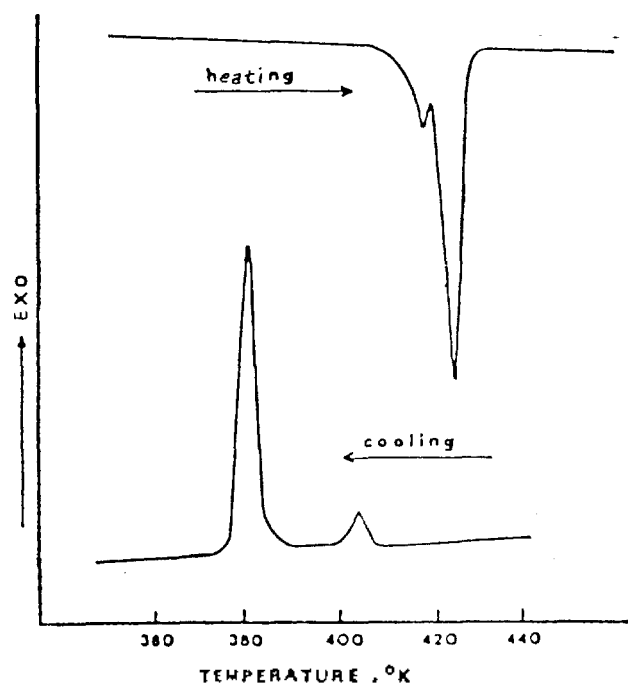


Figure 5. DSC thermogram of the Series II compound with $x = \text{NO}_2$. Heating and cooling rates were $10^\circ\text{C}/\text{min}$.

spacers were higher than those with odd-numbered ones. This could be taken as an indication that the mesophases originating from the compounds having even numbered polymethylene spacers are more highly ordered than those with an odd number of methylenes. Similar trends have been reported for many other series of compounds^{15,16}.

Properties of the Compounds of Series II. The compounds of this series have different substituents at the para position of the terminal phenyl units. The hexamethylene group was the flexible spacer for all of these compounds. The influence of terminal substituents on liquid crystal behavior has been systematically evaluated for many other series of compounds^{6,17}, but very few studies describing the structure-property relationship for the type of compounds studied here have been reported in detail.

The DSC thermograms of the compound with phenyl substituents contained three sharp endotherms on the heating cycle and three exotherms on cooling, leading to the conclusion that it is an enantiotropic liquid crystal. However, the

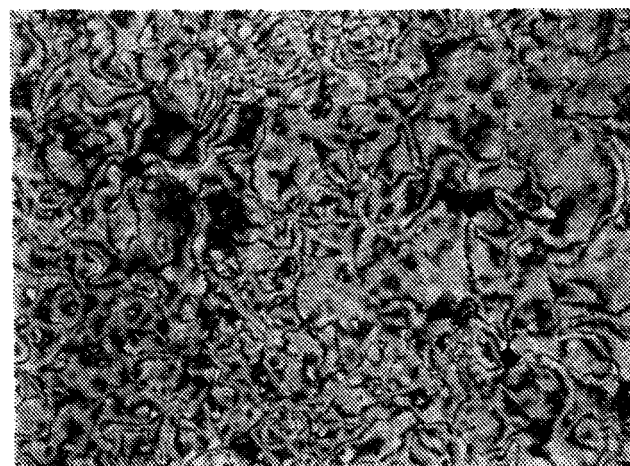
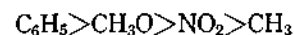


Figure 6. Photomicrograph of the Series II compound with $x = \text{NO}_2$ taken at 128°C (magnification; $300\times$) on cooling cycle.

compounds with nitro, methoxy or methyl substituents were monotropic and showed the mesophase transitions only on cooling, see Figure 5. The rest of the compounds were found to be nonliquid crystalline. The compound with $x = \text{phenyl}$ formed S_A and nematic phases enantiotropically. The optical textures observed for the three monotropic compounds were those typical of a nematic mesophase, see Figure 6. Even though the reason why the compounds with H, Cl and CN substituents didn't form a mesophase is not clear, a few conjectures can be made. The nitrile substituent is expected to strongly withdraw electrons from the mesogenic units reducing the molecular polarizability. This, in turn, disfavors the formation of a mesophase. On the other hand, the high values of ΔH_m 's of the compounds with $x = \text{H}$ or Cl compared with others in this series seem to be at least one of the reasons why the compounds didn't form the mesophase. Judged by isotropic-to-mesophase transition temperatures, the ability of the substituent to stabilize the mesophase followed the order shown below;



Either enhanced polarizability or increased polarity or lengthening of the rigid-rodlike structure by the substituents or a combination thereof appears to be the most important

factors in stabilization of the nematic phase⁶. The above order is in fair agreement with those observed for other types of compounds.

Conclusions

The following conclusions can be drawn from this study:

- (1) The compounds with $n=2, 3, 7, 9$ and 10 of Series I were monotropic, while the others were enantiotropic.
- (2) As the polymethylene spacer becomes longer, the compound tends to form a smectic phase.
- (3) The melting and isotropic transition temperatures of the compounds of Series I decreased with the central spacer length. The decrease showed an odd-even relationship.
- (4) Only the compounds with phenyl, nitro, methoxy and methyl substituent of Series II exhibited mesophases. The monotropic compounds formed only nematic phase. However, the phenyl substituted compound was enantiotropic and formed both smectic A and nematic phases.
- (5) The ability of the substituent to stabilize the mesophase of Series II compounds was in the following order;



Acknowledgement. The authors are grateful to the Korea Science and Engineering Foundation for the support of this research. They are also thankful to Dr. Robert Ausubel for his many useful suggestions in the preparation of this article.

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The Thermal Properties of PVC-Ni Composite Materials

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(Received November 23, 1984)

The glass transition temperature, dynamic shear moduli, and bulk viscosities of PVC, filled with nickel particles, were investigated. The glass temperature of the composite increased with increasing filler concentration. The data were interpreted by assuming that the interaction between filler particles and the polymer matrix reduces molecular mobility and flexibility of the polymer chains in the vicinity of the interfaces. The relative modulus for the PVC/Ni composite system followed the Kerner equation. The relative viscosities were strongly temperature dependent and did not agree with the conventional viscosity predictions for suspensions. It is suggested that the filler has a twofold effect on the viscosity of the composite materials; one is due to its mechanical presence and the other is due to modification of part of the polymer matrix caused by interaction. This phenomenon is approximately bounded by Kerner's predictions for suspensions.

1. Introduction

The glass transition temperature, T_g , of metal-filled polymers, the extent of interaction between polymeric matrix

and metallic filler and its effect on the thermal property of the composite materials were investigated to pursue the mechanism of the composite formation.

Since the thermal property, especially the glass transition