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Liquid Crystalline State in Hexakis[4-(4-cyano)biphenoxy]- and Hexakis[4-(phenylazo)phenoxy]cyclotriphosphazenes

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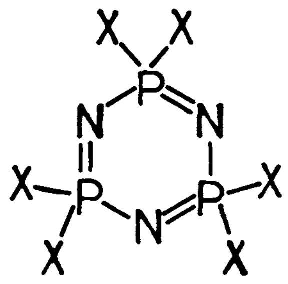
We synthesized hexakis[4-(4-cyano)biphenoxy]cyclotriphosphazene(HCBCTP) and hexakis[4-(phenylazo)phenoxy]cyclotriphosphazene(HPAPCTP) and found a nematic phase between 529 and 488 K in the cooling process of HCBCTP by DSC measurements and polarizing microscope observations, but no mesomorphic state was found in HPAPCTP.

Cyclotriphosphazenes are cyclic compounds of the general formula $(PNX_2)_3$, in which four-coordinated phosphorus atoms alternate regularly with nitrogen atoms in a ring. They are illustrated in Fig. 1.

Singler et al.[1)] tried the introduction of a mesogen to X in the cyclotriphosphazene as a model compound for polymeric liquid crystals. They observed liquid crystal phase in hexakis[2-(4-(4-butoxyphenylazo)-phenoxy)ethoxy]cyclotriphosphazene($X=OCH_2CH_2O\Phi\Phi C_4H_9$)(HBPAPECTP) between 405 and 461 K by use of DSC and polarizing microscope. But they have long alkyl ether chains between phosphorus atom and the rigid core of mesogen. We considered the introduction of mesogen without the flexible chain to X. Such cyclotriphosphazenes are expected to make new liquid crystals on the basis of molecular shape considerations, because the mesogen is more rigid than that of HBPAPECTP. For this purpose we prepared two new organocyclotriphosphazenes of hexakis[4-(4-cyano)biphenoxy]cyclotriphosphazene (HCBCTP)($(PN(O\Phi\Phi CN)_2)_3$ and



X = OΦΦCN(HCBCTP) and

OΦNNΦ(HAPACTP)

Fig. 1. Chemical structure of cyclotriphosphazenes.

hexakis[4-(phenylazo)phenoxy]cyclotriphosphazene(HPAPCTP)$(PN(O\Phi NN\Phi)_2)_3$ as shown in Fig.1 and studied the phase transition by DSC measurements and polarized microscope observations.

HCBCTP and HPAPCTP were synthesized by substitution reaction of hexachlorocyclotriphosphazene(supplied from Nihon Seika Co., Ltd.) and sodium salts of the corresponding aryl alcohol in dioxane solution. Each sodium salt was prepared from sodium metal and 4-cyanobiphenoxy-4'-ol (supplied from Chisso Co., Ltd.) or 4-hydroxyazobenzene(Tokyo Kasei Co., Ltd.). The products obtained were recrystallized three times from chloroform for HCBCTP and from benzene-petroleum ether(1:1) solution for HPAPCTP. The compounds purified were identified as objectives by IR, ^{1}H and ^{31}P NMR and TLC, respectively. The IR spectra of HCBCTP and HPAPCTP showed the existence of -P=N- bond at 1310 cm^{-1} and typical C-H aromatic vibration around 3000 cm^{-1}. The existence of N=N bond (1420 cm^{-1}) for HPAPCTP and CN bond (2250 cm^{-1}) for HCBCTP was also shown in the spectra. The ^{1}H NMR spectra for HCBCTP and HPAPCTP showed the existence of biphenyl (7.12-7.80, m, ArH) and phenyl (7.16-7.78, m, ArH) protons in $CDCl_3$. The ^{31}P NMR spectra were measured in THF with the external reference of aqueous H_3PO_4. In the spectra, only one sharp singlet was observed at 9.7 ppm and 9.4 ppm in HCBCTP and HPAPCTP, respectively. This indicates that the environment of each P atom of both compounds is equivalent and consequently the replacement of chlorine with mesogen is complete.

Phase transitions were measured with a differential scanning calorimeter(Seiko Instruments DSC-210) at a heating/cooling rate of 5 K min^{-1} in a temperature range from 300 K to over the melting point. The texture of

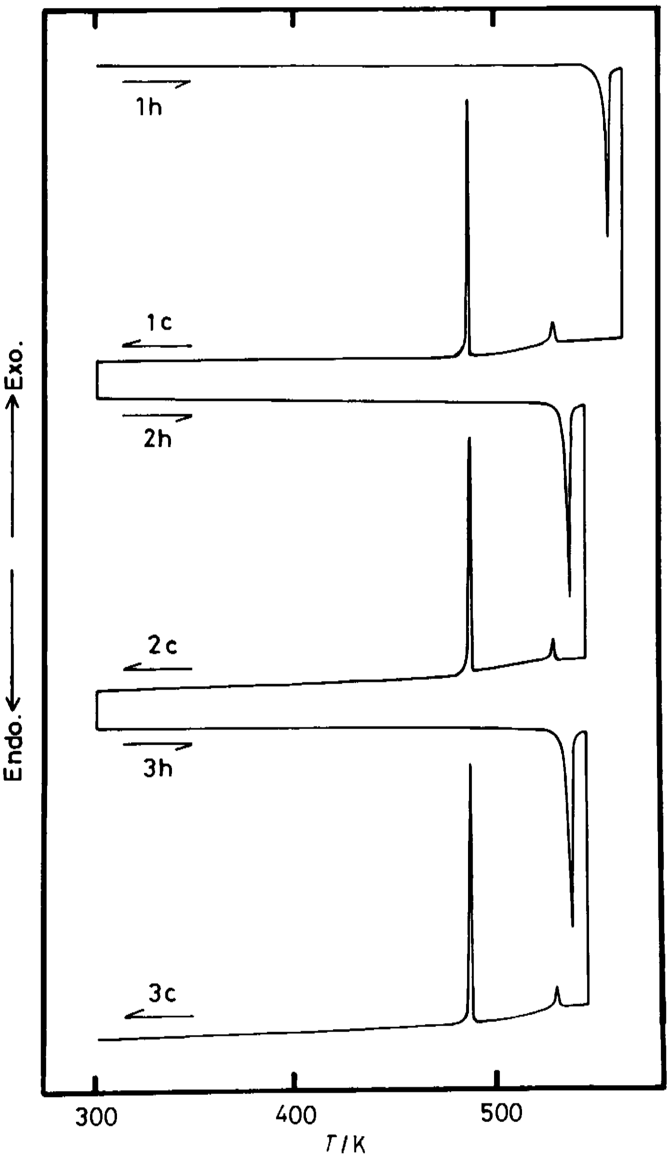


Fig. 2. DSC curves of HCBCTP.

liquid crystal phase was observed by a polarizing microscope(Nikon, Optiphoto-pol XTP-11) equipped with a Mettler FP-2 hot stage at a heating/cooling rate of 5 K min^{-1} under a crossed polarizer.

Figure 2 gives the DSC curves of HCBCTP and the phase transition parameters are shown in Table 1. One endothermic peak corresponding to melting is observed at 555 K in the first heating process. On cooling from melting, two exothermic peaks are found at 529 and 488 K. Entropy of the high-temperature phase transition(ΔS = 8.3 J $K^{-1}mol^{-1}$) is much smaller than that of the low-temperature phase transition(ΔS = 118 J $K^{-1}mol^{-1}$). This result suggests that the metastable intermediate phase is highly disordered with its disorder close to the isotropic liquid state. In the second heating process, only one endothermic peak corresponding to melting was observed at 536 K. In the second cooling process the peaks observed are almost the same as those of the first cooling process. Similar curves as those of the second processes are obtained in third thermal processes. The difference between the melting temperatures of the first and other heating processes are considered to show that the crystal structure of as-grown crystals are different from that of the crystals after melting. The polarizing microscope photograph of HCBCTP at 513 K is shown in Fig. 3 under crossed nicole. The schlielen

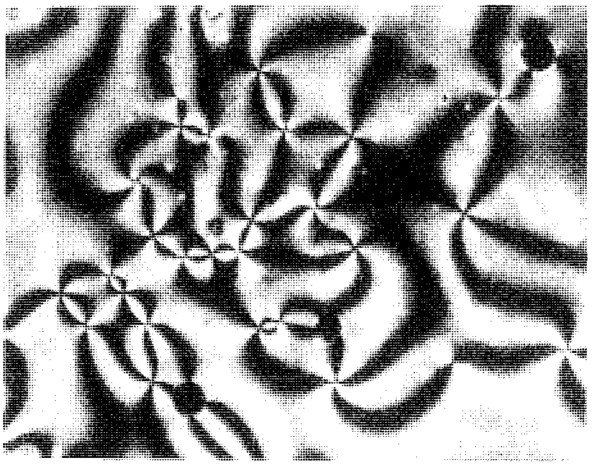


Fig. 3. Polarizing microscope photograph of HCBCTP at 513 K.

Table 1. Phase Transition Parameters of HCBCTP and HPAPCTP

Compounds		T_m	ΔH_m	ΔS_m		T_{I-N}	T_f	ΔH_{I-N}	ΔH_f	ΔS_{I-N}	ΔS_f
		K	kJ mol^{-1}	J $K^{-1}mol^{-1}$		K	K	kJ mol^{-1}	kJ mol^{-1}	J $K^{-1}mol^{-1}$	J $K^{-1}mol^{-1}$
HCBCTP	1h	555	72.7	131	1c	530	487	4.4	57.5	8.3	118
	2h	536	70.9	132	2c	529	488	4.0	56.6	7.6	116
	3h	537	70.0	130	3c	529	488	4.1	57.0	7.8	117
HPAPCTP	1h	454	65.1	143	1c		415		57.7		139
	2h	453	64.2	142	2c		414		56.8		137

nh: on the nth heating, T_m: melting point, ΔH_m: enthalpy of fusion, ΔS_m: entropy of fusion, nc: on the nth cooling, T_{I-N}: phase transition temperature from isotropic to nematic, T_f: freezing point, ΔH_{I-N}: enthalpy of I-N transition, ΔH_f: enthalpy of freezing, ΔS_{I-N}: entropy of I-N transition, ΔS_f: entropy of freezing.

texture with disclination lines having s=±1/2 and s=±1 is observed being a characteristic of the nematic phase.

Figure 4 gives DSC curves of HPAPCTP and the phase transition parameters are shown in Table 1. One endothermic peak corresponding to melting is observed at 454 K in the first heating process. On the first cooling one exothermic peak corresponding to freezing is observed at 415 K. Consequently, no mesomophic transition was observed in HPAPCTP.

In conclusion this work is the first case of a mesomorphic state of organocyclotriphosphazene with no flexible chain between the P-O linkage and the rigid core of mesogens. In HCBCTP free motion of the mesogen is restricted by the phosphazene ring. Furthermore the aromatic ring of the mesogen and the phosphazene ring in HCBCTP may not be coplaner as is other organocyclotriphosphazene.[2)] Thus molecular shape of the HCBCTP much differs from that of usual liquid crystals, which are composed of a simple lathlike molecule(mesogen) having a rigid core and flexible tail. In order to know the relation between this particular molecular shape and its arrangement in the mesomorphic state we must study the nematic phase of HCBCTP from the structural and optical standpoint. Study of the nematic phase by X-ray scattering and conoscopic observations will be published elsewhere.

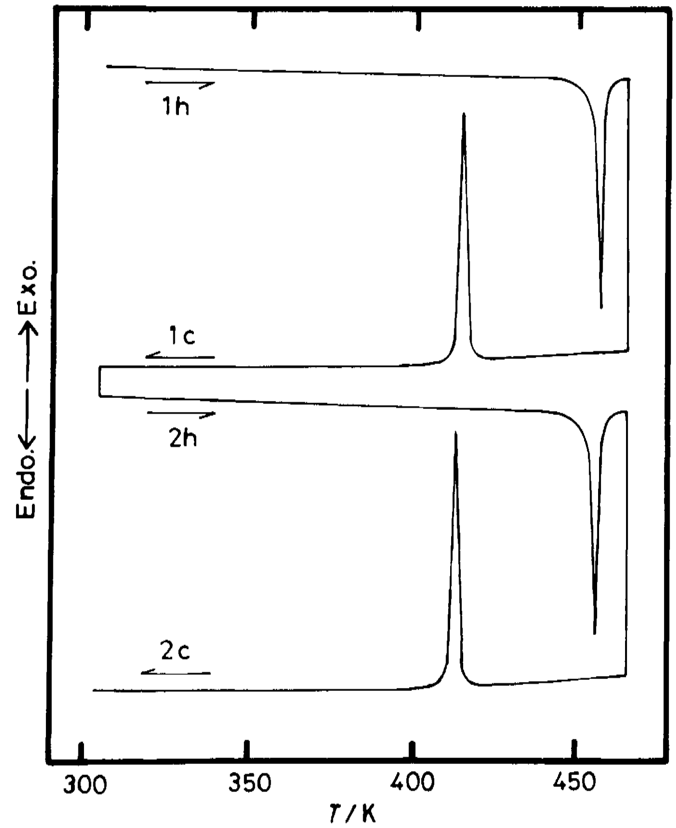


Fig. 4. DSC curves of HPAPCTP.

References

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