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Twist Phase Transition in Poly(*p*-phenylene) Oligomers: Heat Capacity of *p*-Quinquephenyl

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The heat capacity of crystalline *p*-quinquephenyl was measured by adiabatic calorimetry below room temperature. A broad hump was detected around 264 K and attributed to a phase transition, through which an average molecular conformation changes from the planar to the twisted one on cooling. A similar anomaly was also detected for crystalline *p*-sexiphenyl around 295 K by chopped-light ac calorimetry. The broad shape of the thermal anomalies arising from the twist transitions are discussed in relation to the number of possible intramolecular twisting modes. Properties of the twist transition in polymer are discussed on the basis of those of oligomers. Standard thermodynamic functions are tabulated for *p*-quinquephenyl.

Poly(*p*-phenylene) is one of the polymers on which extensive studies have been conducted for physical properties, because of its potential functionalities such as electrical conduction or optical applications.[1—3] In spite of extensive studies, however, even molecular and crystal structures have not been established yet.[4—6] It is now clear that small oligomers (biphenyl through *p*-septiphenyl) crystallize into a monoclinic unit cell with apparently planar conformation at room temperature.[7—10] The planarity is exact for even-membered oligomers in the sense of the site symmetry whereas it is only approximate for odd members. It is widely accepted that the molecules are twisted in an isolated (i.e., gaseous) state due to the steric repulsion between *ortho* hydrogen atoms. This is experimentally observed for biphenyl.[11] On cooling, phase transitions occur in the crystals of the first three members.[12] The molecules resume the alternately twisted conformation below the phase transition.[13—15] The nature of the twist transitions is different for biphenyl and for *p*-terphenyl and *p*-quaterphenyl. More precisely, the transition in biphenyl is of a displacive type associated with soft-modes,[12,16—18] while those in *p*-terphenyl[14,19,20] and *p*-quaterphenyl[15,21] are of an order-disorder type. The planar conformation in *p*-terphenyl and *p*-quaterphenyl crystals at room temperature is a dynamical average of two conformations.[8,9] In the order-disorder twist transition, the pseudo spin variable is a good approximation for the twist of a whole molecule, implying a complete correlation of twisting within a molecule.

For polymers, there is no report of a twist transition. Negative statements are found in some references.[6,10,22,23] The configurational entropy, however, surely prefers the disordered conformation at high temperature, the ordered one at low temperature. It is therefore of great interest to see how the twist transition changes its properties on going to the polymer starting from a small oligomer. Clarifying the point will contribute to establishment of the structure of the polymer to a great extent. This situation leads the authors to extend their study on the twist transitions on small oligomers to longer ones.

The crystal structures of *p*-quinquephenyl, *p*-sexiphenyl, and *p*-septiphenyl are isostructural with monoclinic unit cell of the space group $P2_1/a$.[10] The molecules are seemingly planar and are located on the inversion centers. The thermal ellipsoids of carbon atoms at room temperature are rather elongated normal to the molecular plane, implying the statistically disordered nature of the structure. It is therefore natural to expect a twist transition to exist at a low temperature. Indeed, the existence of the transition was recently suggested for them between room temperature and 110 K, where the space group and the unit cell are different from those at room temperature.[10] The main interests in this paper are as follows: 1. Are there twist transitions in longer oligomers? 2. Does the molecule as a whole play a role of a spin variable in longer oligomers? That is, does the intramolecular correlation of the twisting motions of benzene rings survive in a longer oligomer? 3. How do the properties of the twist transition change with increase in the molecular length? 4. What is the twist transition in the polymer?

Although both calorimetry and diffractometry give crucial information concerning those questions, the former seems more suitable than the latter in this case because of difficulties in crystal growth and variable temperature experiments. In this paper, the results of precise heat capacity measurement on crystalline *p*-quinquephenyl and of ac calorimetry on *p*-sexiphenyl are described and discussed in relation to the above mentioned interests.

Experimental

Powdered colorless specimens of *p*-quinquephenyl and *p*-sexiphenyl were purchased from Tokyo Chemical Industry. They were guaranteed reagent quality of the supplier and were used for experiments without further purification.

For heat capacity measurement by adiabatic calorimetry, the powdered sample of *p*-quinquephenyl was loaded into a gold-plated copper calorimeter vessel. The mass of the sample loaded was 1.2382 g (3.2371 mmol) after the buoyancy correction has been applied for. The vessel was evacuated and sealed after filling with helium gas of 10^5 Pa at room temperature. The sample contributed typically 20% (at room temperature) to the total heat capacity, which includes that of the calorimeter vessel.

The calorimeter vessel was mounted in the laboratory-made adiabatic calorimeter. The details and operation of the adiabatic calorimeter were described elsewhere.[24] The working thermometers attached to the vessel were platinum (Minco, S1055) and germanium (Lake-Shore, GR-200B-500) resistance thermometers, the temperature scales of which are based upon the ITS-90.

To see the presence of a twist transition in crystalline *p*-sexiphenyl, thermal analytical measurement was made on a tiny amount of specimen by using a chopped-light ac calorimeter. The powdered specimen was compressed to a thin pellet. A piece ($1.0\times0.9\times0.04$ mm^3) was cut from the pellet and mounted on a crossing point of thermocouples (13 μm in diameter). The surface of the sample was blackened with thin carbon film. The measurements were done at 1 Hz while slowly heating. The details of the ac calorimeter were also described elsewhere.[25] The ac calorimeter can detect a thermal anomaly with magnitude of about 1 per cent of heat capacity.[26]

Results and Discussion

Heat Capacity and Thermodynamic Functions of *p*-Quinquephenyl. The heat capacity of crystalline *p*-quinquephenyl was measured between 6 and 303 K. While the time required for cooling the calorimeter vessel from room temperature down to 100 K was about 3 h, the times for heating the vessel by about 2 K and for equilibration were 20 min and 10 min, respectively, above 250 K. All the data are plotted in Fig. 1. A broad hump is recognized around 264 K, on which a detailed discussion is given later. Even in the temperature range of the hump, i.e., the transition region, there was no anomalous behavior in reaching thermal equilibrium.

The primary data were smoothed out and extrapolated to the absolute zero consistently with the Debye law in the low temperature limit. The smoothed heat capacity was integrated to yield the standard thermodynamic functions, which are given at selected temperatures in Table 1.

It is of interest from Fig. 1 that the heat capacity at a given temperature increases regularly on the elongation of the molecular size. For example, at 300 K, the heat capacity increases by about 90 J K^{-1} mol^{-1}. If this trend would hold over the entire temperature range except for those in the vicinities of phase transitions, the molar heat capacity of poly(*p*-phenylene) with perfect crystallinity might be determined. To see more details, the differences in molar heat capacity are plotted and compared with the reported heat capacity of poly(*p*-phenylene)[27] in Fig. 2. All the differences are favorably compared between 60 and 140 K. The differences between *p*-quinquephenyl and *p*-quaterphenyl and between *p*-quaterphenyl and *p*-terphenyl are also in good agreement between 10 and 50 K. These features are reasonable because the temperature regions are outside the transition regions. On the other hand, the differences become significant at higher temperatures. This fact results from thermally activated reorientational motion of the phenyl rings about the figure axis. As for the comparison between the differences and the reported heat capacity of the polymer, the agreement is only semi quantitative.

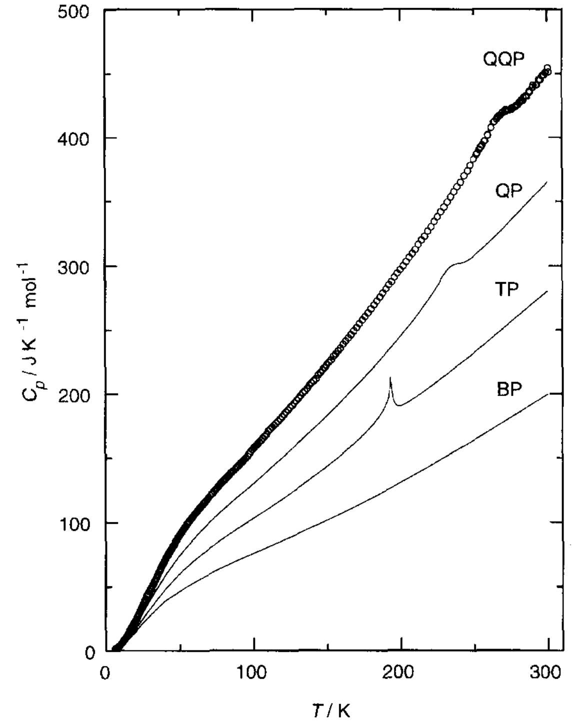

Fig. 1. Measured molar heat capacities (circle) of *p*-quinquephenyl (QQP). Heat capacities of biphenyl (BP),[18] *p*-terphenyl (TP),[19] and *p*-quaterphenyl (QP)[21] are also shown for comparison.

The heat capacity of highly anisotropic crystal attracted theoretical and experimental interests in the past.[28] Crystalline polymer was recognized as a model system of a quasi-one-dimensional crystal. In one respect, poly(*p*-phenylene) is ideal among the polymers so far studied because the backbone of this polymer is really straight in contrast to the zigzag backbone of polyethylene, the polymer most extensively studied. Most theoretical models predict the cubic and linear temperature dependence of heat capacity of one-dimensional lattice at low enough and moderate temperatures, respectively. The models, however, consider only acoustic modes arising from translational degrees of freedom of monomers. The classical (high-temperature) value of the contribution of the acoustic modes is $3R\approx25$ J K^{-1} mol^{-1}. A seemingly linear dependence above 100 K is therefore beyond such models. Indeed, the contribution of the intramolecular vibrations amount to ca. 50 J K^{-1} mol^{-1} at room temperature,

Table 1. Standard Thermodynamic Quantities of *p*-Quinquephenyl

T	C_p°	$[H^\circ(T) - H^\circ(0)]/T$	$S^\circ(T) - S^\circ(0)$	$-[G^\circ(T) - H^\circ(0)]/T$
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}
10	5.11	1.35	1.80	0.45
20	22.92	7.28	10.24	2.96
30	47.20	16.63	24.22	7.60
40	70.43	27.19	41.00	13.81
50	89.94	37.86	58.89	21.03
60	106.23	47.93	76.77	28.83
70	120.05	57.27	94.21	36.94
80	132.49	65.91	111.06	45.15
90	144.50	73.97	127.36	53.39
100	156.92	81.64	143.22	61.58
110	170.17	89.08	158.79	69.71
120	183.09	96.38	174.16	77.78
130	195.58	103.53	189.31	85.77
140	208.7	110.57	204.3	93.7
150	222.6	117.57	219.2	101.6
160	236.8	124.58	234.0	109.4
170	251.4	131.61	248.8	117.2
180	266.1	138.67	263.5	124.9
190	281.1	145.77	278.3	132.6
200	296.4	152.92	293.1	140.2
210	312.1	160.13	308.0	147.9
220	328.5	167.40	322.9	155.5
230	345.5	174.77	337.9	163.1
240	363.5	182.26	352.9	170.7
250	381.9	189.87	368.1	178.3
260	402.6	197.64	383.5	185.9
270	418.3	205.6	399.0	193.5
280	425.3	213.3	414.4	201.1
290	437.4	220.8	429.5	208.7
300	451.7	228.3	444.6	216.3
298.15	449.2	226.9	441.8	214.9

while assuming the same vibrational frequencies as those of benzene molecule.[29] Besides, the models do not consider the librational lattice mode, the frequencies of which lie below a few ten's cm^{-1} for poly(*p*-phenylene).[30]

The temperature dependence shown in Fig. 2 below about 50 K is weaker than of square. Similar temperature dependence is observed in other linear polymers.[31] The temperature region where the cubic dependence corresponding to the Debye law is realized is below about 5 K for them.

Thermal Anomaly in Crystalline *p*-Quinquephenyl. Figure 3 shows an enlarged plot of measured heat capacities over the broad hump. The hump suggests the existence of a phase transition of higher-order. Considering the similarity in the room temperature crystal structure between *p*-quinquephenyl[10] and the smaller polyphenyls,[7—9] it is natural to suspect a twist transition in crystalline *p*-quinquephenyl. Since the temperature of the twist transition shifts upward on elongation of the molecular size in the smaller *p*-polyphenyls (see Fig. 6), the transition temperature in *p*-quinquephenyl is expected to lie above 250 K. The detected thermal anomaly is consistent with this expectation. It is thus natural to assign the thermal anomaly to a twist transition in crystalline *p*-quinquephenyl.

A similar broad hump was observed in *p*-quaterphenyl[21] and 4,4‴-difluoro-*p*-quaterphenyl,[32] where other experiments[33—35] show that the transition temperature agrees with the temperature of the broad maximum of the hump after subtracting a normal heat capacity. It is usually hard to estimate the normal curve (baseline) in cases where a thermal anomaly extends over wide temperature range as in the present case. In the previous studies on unsubstituted and fluorine-substituted *p*-polyphenyls,[18—21,32,36] the baseline was assumed to be a smooth interpolation between low- and high-temperature sides of the anomaly.

The baseline is thus tentatively drawn as shown in Fig. 3, though it is unclear at which temperature the high-temperature tail completes. The subtraction of this baseline gives the apparent excess heat capacities shown in Fig. 4. The temperature of the twist transition is determined as (264±1) K from the temperature of the maximum. The enthalpy and entropy of transition are estimated by integrating the excess heat capacities as (450±10) J mol^{-1} and (1.7±0.1) J K^{-1} mol^{-1}, respectively. The entropy of transition is comparable with those in *p*-terphenyl[19] and *p*-quaterphenyl[21] that show twist transitions of the order-disorder type.

Most theories of phase transition predict a singular behav-

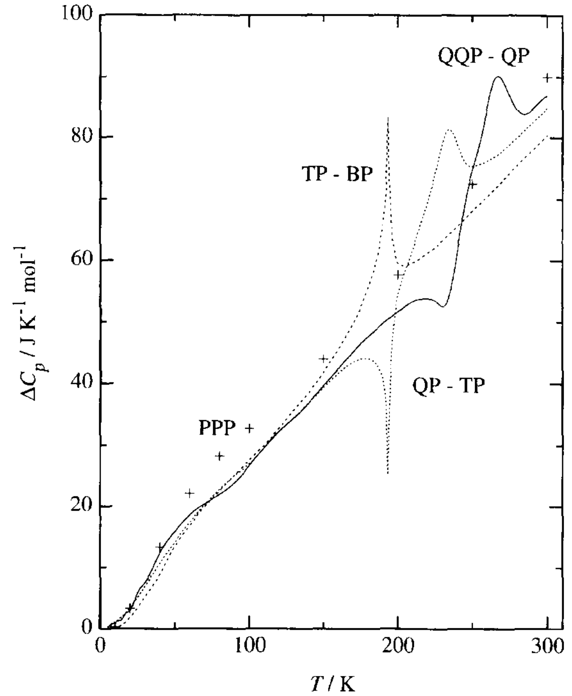

Fig. 2. Difference in molar heat capacities corresponding to the contribution of a phenyl ring. The difference between *p*-terphenyl (TP)[19] and biphenyl (BP)[18] is designated as TP−BP. Other designations use the abbreviation QP for *p*-quaterphenyl[21] and QQP for *p*-quinquephenyl. The literature values of the heat capacity per mole of monomer of poly(*p*-phenylene) (PPP)[27] are plotted by plus signs.

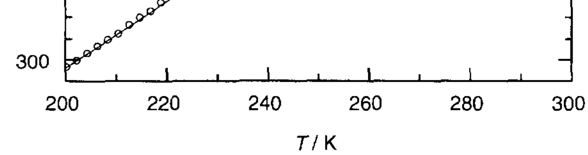

Fig. 3. Measured heat capacities of crystalline *p*-quinquephenyl around the thermal anomaly due to the twist transition. A baseline for separating the excess heat capacity is drawn by solid line.

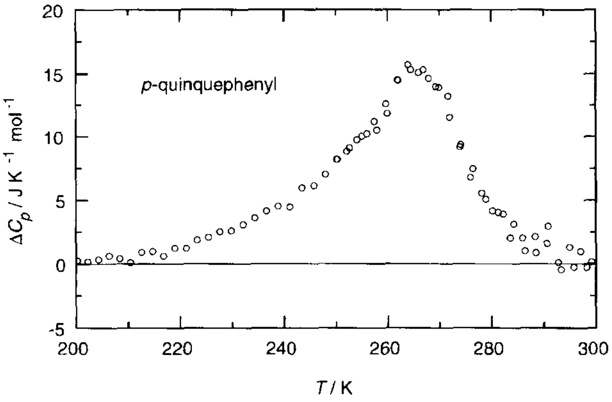

Fig. 4. Excess heat capacities due to the twist transition in crystalline *p*-quinquephenyl.

ior at a critical point (phase transition temperature) for heat capacity. On the other hand, the thermal anomaly observed in this study is broad. Similar broad anomalies were detected for twist transitions in crystalline biphenyl,[18] *p*-quaterphenyl,[21] and 4,4‴-difluoro-*p*-quaterphenyl,[32] whereas a sharp one was detected for *p*-terphenyl[19] and 4,4″-difluoro-*p*-terphenyl.[35] The nature of the twist transition mentioned above covers displacive and order-disorder types. Since the shape of the thermal anomaly depends on the parity of the number of phenyl rings in a molecule rather than on the nature of the twist transition, the authors previously concluded that the effect is a type of even-odd effect.[21,32] The present result, however, clearly contradicts our earlier conclusion. Some reconsideration is necessary.

The present result implies that *p*-polyphenyls larger than *p*-quaterphenyl exhibit a broad anomaly at the twist transition. To see what type of twisting mode is possible, the presentation of the point group using twistings of the rings as a basis set is decomposed into irreducible presentations. The symmetry D_{2h}, which is the point group of the planar conformation in a high-temperature phase, is assumed. The result is shown in Table 2. The number of the C–C bonds at which the twist occurs is also included in the table. It is expected that the height of potential barrier for the mode is roughly proportional to the number of such C–C bonds. The number of the C–C bonds is always the largest for the mode relevant to the twist transition because the twisting mode reported for the low-temperature phase is of alternate twisting.[13—15] For biphenyl, there is only one twisting mode, which is the mode relevant to the twist transition. *p*-Terphenyl has two internal twisting modes, which have the same numbers of the twisting C–C bonds. A different feature is seen in molecules longer than *p*-quaterphenyl. There exist twisting modes with smaller numbers of the twisting C–C bonds than the number in the mode relevant to the twist transition. The authors recognized this fact previously,[21] but thought this was of secondary importance. Considering the broad thermal anomalies for *p*-quaterphenyl and *p*-quinquephenyl, the existence of competitive twisting mode(s) with smaller number(s) of the twisting C–C bonds seems essential. That is, a twist transition in longer *p*-polyphenyls, if present, will bring about a broad thermal anomaly. It should be noted that the discussion given here merely considers possible twisting modes. A microscopic model to explain the shape of the thermal anomaly is left for future theoretical studies.

Thermal Anomaly in Crystalline *p*-Sexiphenyl. The temperature dependence of the heat capacity of crystalline *p*-sexiphenyl is measured by chopped-light ac calorimetry us-

Table 2. Possible Twisting Modes in *p*-Polyphenyls. The Number of the C–C Bonds Where the Twist Occurs for the Mode is Designated as *N*

Molecule	Symmetry	Twist mode	*N*
Biphenyl	$\mathrm{A_u}$	(+)–(−)	1
p-Terphenyl	$\mathrm{A_u}$	(+)–(0)–(−)	2
	$\mathrm{B_{1g}}$	(+)–(−)–(+)	2
p-Quaterphenyl	$\mathrm{A_u}$	(+)–(+)–(−)–(−)	1
		(+)–(−)–(+)–(−)	3
	$\mathrm{B_{1g}}$	(+)–(−)–(−)–(+)	2
p-Quinquephenyl	$\mathrm{A_u}$	(+)–(+)–(0)–(−)–(−)	2
		(+)–(−)–(0–(+)–(−)	4
	$\mathrm{B_{1g}}$	(+)–(+)–(−)–(+)–(+)	2
		(+)–(−)–(+)–(−)–(+)	4
p-Sexiphenyl	$\mathrm{A_u}$	(+)–(+)–(+)–(−)–(−)–(−)	1
		(+)–(0)–(−)–(+)–(0)–(−)	5
		(+)–(−)–(+)–(−)–(+)–(−)	5
	$\mathrm{B_{1g}}$	(+)–(+)–(−)–(−)–(+)–(+)	2
		(+)–(0)–(−)–(−)–(0)–(+)	4

ing a compressed pellet of the powder specimen. Because of poor sample purity (chemical and/or physical), poor thermal diffusivity of the pellet, and poor thermal contact between the pellet and the thermocouple, the result is regarded as of thermal analysis, but shows a hump centered around 295 K, as shown in Fig. 5. Besides the same discussion as made for *p*-quinquephenyl, the alternate twist mode of the molecule results in the change in the site symmetry. It is therefore natural to attribute the hump to a twist transition in crystalline *p*-sexiphenyl. The broad shape is consistent with the discussion made in the previous section for *p*-quinquephenyl, though the observed broadness may result from the insufficient purity and/or crystallinity. It is impossible to estimate the enthalpy and/or entropy of this transition from the present results.

Molecular dynamics simulation on *p*-sexiphenyl cluster has been reported by Socci et al.[23] Although they claimed that there was no symptom of a double well in the potential energy curve for the twisting motion, the reported temperature dependence (though only two points at 300 K and 400 K) of the squared average of the twist angle at the molecular center is anomalously large in comparison with those reported for smaller *p*-polyphenyls.[35] The large temperature dependence seems to be rationalized if the twist phase transition is assumed to exist between 300 and 400 K in their model. This will be acceptable because the phase transition temperature strongly depends on the details of intermolecular interaction.

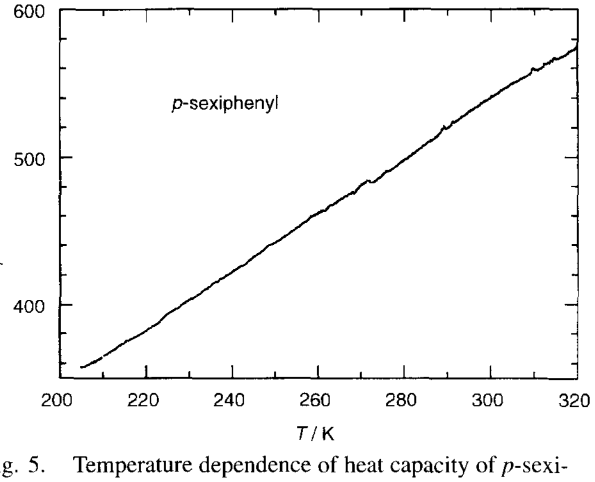

Fig. 5. Temperature dependence of heat capacity of *p*-sexiphenyl measured by ac calorimetry at 1 Hz.

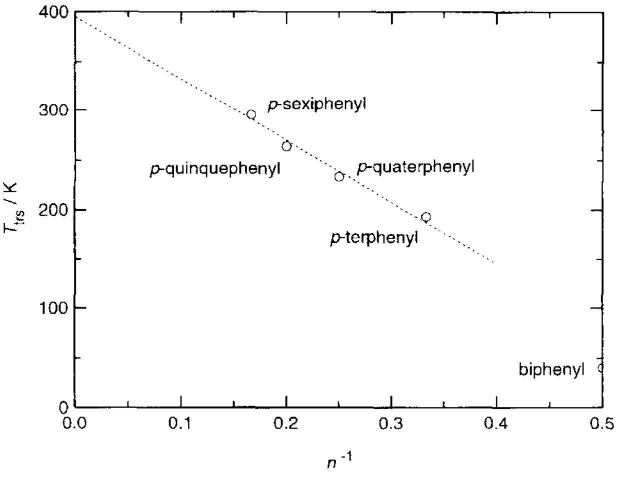

Fig. 6. Twist transition temperature of *p*-polyphenyl oligomers as a function of the inverse of the number of phenyl rings in a molecule (*n*).

Twist Transition in Poly(*p*-phenylene). Now the properties of possible twist transition in poly(*p*-phenylene) are briefly discussed. The configurational entropy surely prefers the disordered (seemingly planar) conformation at high temperature, whereas it prefers the ordered one at low temperature. For this molecular packing of oligomers, the mode of the ordered twist in the polymer is plausibly of the alternate twist. This ordering seems to accompany cell doubling. It is therefore natural to suspect a twist transition in the polymer. The possibility of such a transition is, of course, primarily restricted by the thermal stability of polymer, because the transition temperature shows an upward shift on elongation in oligomers. Apart from details of the transition mechanism, the most naive estimate is obtained from a simple extrapolation shown in Fig. 6. Here the point corresponding to biphenyl (displacive type) is ignored in extrapolation because the mechanism of the twist transition of biphenyl is different from those of others (order-disorder type). A transition temperature of the polymer with infinitely large degree of polymerization is roughly estimated as (395±10) K from the figure. Even though this estimate is too low, it is hard to draw an extrapolating curve that gives a "transition temperature" higher than the limit of thermal stability. It is therefore concluded that the twist transition will exist even in crystalline poly(*p*-phenylene).

The excess entropy (or entropy of transition) per molecule is roughly constant for *p*-terphenyl,[19] *p*-quaterphenyl,[21] and *p*-quinquephenyl. If this holds for the polymer, the entropy of transition (per monomer) is effectively zero for a polymer even if the twist transition survives. The correlation (or coherence) within a molecule, however, will diminish on going to a high polymer, as can be seen in the broadening of the thermal anomaly discussed above. The fascinating scenario, thus, seems plausible, that is, at some degree of polymerization, the monomer begins to behave as a basic unit of crystal. The entropy of transition will grow at the same time because the ideal value is $R\ln 2 \approx 5.8\ \mathrm{J\,K^{-1}}$ (mol of monomer)$^{-1}$ in this limit. If this is the case, the twist transition will be a direct measure of the "transition" between small molecule and polymeric compound.

Conclusion

Heat capacity of crystalline *p*-quinquephenyl was measured by adiabatic calorimetry between 6 and 303 K. A broad hump due to a twist transition was detected around 264 K. A similar transition was also detected for crystalline *p*-sexiphenyl around 295 K by chopped-light ac calorimetry. The broad shapes of the thermal anomalies due to the twist transitions are discussed in relation to the number of possible intramolecular twisting modes. Properties of the twist transition in polymer are discussed on the basis of those of oligomers. Standard thermodynamics quantities are tabulated for crystalline *p*-quinquephenyl.

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