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The Effect of the Polymer Backbone on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers

By

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ABSTRACT

Poly(ephichlorohydrin) (PECH) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing pendant mesogenic units separated from the main chain through spacers of zero to ten methylene units were synthesized and characterized in order to test the "spacer concept." Both polymers were modified by phase transfer catalyzed esterifications of the chloromethyl groups (PECH) or the bromobenzyl groups (brominated PPO) with potassium ω-(4-oxybiphenyl)alkanoates and potassium ω-(4-methoxy-4'-oxybiphenyl)-alkanoates. While PPO required ten methylene units as spacer and 4,4'-methoxybiphenyl as mesogen to present thermotropic liquid mesomorphism, PECH required no spacer.

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THE EFFECT OF THE POLYMER BACKBONE ON THE THERMOTROPIC BEHAVIOR OF SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

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SYNOPSIS

Poly(epichlorohydrin) (PECH) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) containing pendant mesogenic units separated from the main chain through spacers of zero to ten methylene units were synthesized and characterized in order to test the "spacer concept." Both polymers were modified by phase transfer catalyzed esterifications of the chloromethyl groups (PECH) or the bromobenzyl groups (brominated PPO) with potassium ω-(4-oxybiphenyl)alkanoates and potassium ω-(4-methoxy-4'-oxybiphenyl)-alkanoates. While PPO required ten methylene units as apacer and 4,4'-methoxybiphenyl as mesogen to present thermotropic liquid mesomorphism, PECH required no spacer.

INTRODUCTION

Since Finkelmann and Ringsdorf introduced the spacer concept, it has been well accepted that a requirement for obtaining thermotropic side-chain liquid crystalline polymers is that a flexible spacer must be introduced to partially decouple the mobility of the main chain from that of the mesogenic groups (1-4). Without a spacer, mesophase formation would require that the polymer backbone be significantly distorted from its normal random coil conformation. At the same time, the backbone imposes a steric hindrance on the packing of the mesogens. For this reason, most polymers with the mesogenic groups directly attached to the backbone are amorphous (5). There are however several exceptions to this rule, most of which are listed in Table I, together with their phase transitions. Why is this? It must certainly be true that the motions of the mesogen must be decoupled from those of a rigid polymer backbone. But what about very flexible polymer backbones? We propose that such a backbone may itself act as a flexible spacer.

Table I demonstrates that most liquid crystalline polymers lacking a spacer are formed from a flexible polyacrylate backbone. In contrast, the methyl substituent in polymethacrylate backbones both reduce main chain mobility and imposes additional steric barriers to mesophase formation. Therefore, successful liquid crystalline formation of polymethacrylates has been achieved only when the anisotropy of the mesogen is increased by increasing the number of stiff and highly polarizable units that it contains. This in turn enlarges the mesogen, and is most frequently achieved by attaching a polar substituent para to the polymerizable group of the monomer.

A review of the literature demonstrates some trends concerning the effect of the polymer backbone on the thermotropic behavior of side-chain liquid crystalline polymers. In comparison to low molar mass liquid crystals, the thermal stability of the mesophase increases upon polymerization (3,5,18). However, due to increasing viscosity as the degree of polymerization increases, structural rearrangements are slowed down. Perhaps this is why the isotropization temperature increases up to a critical value as the degree of polymerization increases (18).

There are also some trends when looking at the main chain flexibility. Table II demonstrates that when the main chain flexibility decreases from cyanobiphenyl containing polymethacrylates to polysiloxanes, not only does the Tg drop, but the isotropization temperature increases. However, the trend is the opposite when the mesogen is methoxyphenyl benzoate (18). Therefore, this effect of the main chain flexibility is still ambiguous.

In order to determine the necessity and/or the length of the spacer that is required to achieve liquid crystalline behavior from flexible vs. rigid polymers, we have introduced mesogenic units to the backbones of a rigid [poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)] and a flexible [poly(epichlorohydrin) (PECH)] polymer through spacers of from 0 to 10 methylene groups via polymer analogous reactions.

The synthetic procedure used for the chemical modification of PPO involved in the first step the radical bromination of PPO methyl groups to provide a polymer containing bromobenzyl groups. The bromobenzyl groups were then esterified under phase-transfer-catalyzed (PTC) reaction conditions with potassium 4-(4-oxybiphenyl)butyrate, potassium 4-(4-methoxy-4'-oxybiphenyl)butyrate, potassium 5-(4-oxybiphenyl)valerate, potassium 5-(4-methoxy-4'-oxybiphenyl)valerate, potassium 11-(4-oxybiphenyl)undecanoate, and potassium 11-(4-methoxy-4'-oxybiphenyl)-undecanoate.

PECH was modified under similiar reaction conditions, except that dimethylformamide (DMF) was used as the reaction solvent. In addition, the phase-transfer-catalyzed etherification of the chloromethyl groups of PECH with sodium 4-methoxy-4'-biphenoxide was used to synthesize PECH with direct attachment of the mesogen to the polymer backbone. Esterification routes of both PPO and PECH are presented in Scheme I.

The attachment of mesogenic units to a polymer backbone via polymer analogous reactions is not a new concept, although they are much less frequently used than the polymerization of mesogen containing monomers. Liquid crystalline polyacrylates, polymethacrylates, and polyacrylamides have been prepared by conventional esterification or amidation of poly(acryloyl chloride) and poly(methacryloyl chloride) with a mesogenic alcohol or amine in the presence of triethylamine (8,21,22). Similiarly, liquid crystalline polyacrylates, polymethacrylates, and polyitaconates have been prepared by phase-transfer-catalyzed reactions on the sodium sats of the corresponding polycarboxylates (23-25). In addition, alternating poly(methylvinylether-co-maleate) copolymers were prepared by the PTC reactions of poly(methylvinylether-co-disodium maleate) with mesogen containing bromoalkylesters (26). The most important use of this class of reactions, however, is in the preparation of liquid crystalline polysiloxanes, which cannot be obtained by any other method. We have recently summarized the work on the preparation of liquid crystalline polysiloxanes (19), which involves the platinum catalyzed hydrosilation reaction of vinyl substituted mesogenic molecules with poly(hydrogen methylsiloxane) or its copolymers.

Lastly, it was demonstrated with PPO substituted with a series of alkyl side-chains as we have here, that the glass transition temperature decreases with an increase in the side-chain length (28). At the same time, the Tg's of the more flexible side-chain liquid crystalline polymers investigated to date are always much higher than those of the corresponding polymers without the mesogenic side-chains (3). Therefore, it is quite likely that we may obtain side-chain liquid crystalline polymers of approximately the same Tg from PPO and PECH.

EXPERIMENTAL

The starting polymers were commercial products purified by precipitation with methanol from chloroform solutions: PECH (B. F. Goodrich, $\bar{M}n$=873,000, $\bar{M}w$=10,250,000); PPO (Aldrich, $\bar{M}n$=19,000, $\bar{M}w$=49,000).

The mesogenic units with methylenic spacers were prepared by reacting the sodium salt of either 4-methoxy-4'-hydroxybiphenyl or 4-phenylphenol with a bromoester in DMF at 82°C for at least 4 hours in the presence of tetrabutylammonium hydrogen sulfate (TBAH) as phase transfer catalyst. In this way, ethyl 4-(4-oxybiphenyl)butyrate, ethyl 4-(4-methoxy-4'-oxybiphenyl)butyrate, ethyl 4-(4-oxybiphenyl)valerate, ethyl 4-(4-methoxy-4'-oxybiphenyl)valerate, n-propyl 4-(4-oxybiphenyl)undecanoate and n-propyl 4-(4-methoxy-4'-oxybiphenyl)undecanoate were obtained. These esters were hydrolyzed with base and acidified to obtain the carboxylic acids. The corresponding potassium carboxylates were obtained by reaction with approximately stoichiometric amounts of potassium hydroxide. Experimental details of these syntheses will be described elsewhere (27).

Bromobenzyl groups were introduced into PPO by radical bromination of the methyl groups. The PPO bromobenzyl groups and PECH chloromethyl groups were then esterified under phase-transfer-catalyzed reaction conditions with the potassium carboxylates just described. This procedure has been described previously (29). The sodium salt of 4-methoxy-4'-hydroxybiphenyl was also reacted with PECH (no spacer).

Thermal analysis was performed with a Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a Perkin-Elmer TADS thermal analysis data station. Heating and cooling rates were 20°C/min, and Indium was used as the calibration standard. All samples were heated to just above Tg and quenched before the first heating scan was recorded. A Carl Zeiss optical polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor was used to analyze the anisotropic textures.

Table III summarizes the reaction conditions and the results of the substitution of PPO for all reactions performed, while Table IV presents the results for the modification of PECH.

RESULTS AND DISCUSSION

The synthetic route used for the chemical modification of PPO and PECH is outlined in Scheme I. The results of the esterification reactions of PPO and of PECH are summarized in Tables III and IV respectively. It was previously shown that the only available procedure for the nucleophilic substitution of bromomethylated PPO was by solid-liquid phase-transfer reactions in aprotic nonpolar solvents (29), since PPO is not soluble in aprotic dipolar solvents which are required for conventional nucleophilic substitutions. In both cases, it was necessary to use elevated temperatures (60°C) to obtain good halide displacement. However, it is again demonstrated that PECH is less reactive toward nucleophilic displacement than PPO. Although Me4COOK seems to result in the most efficient substitution, and although the carboxylate nucleophilicities would be expected to change with different spacers, these results are not completely comparable due to different amounts of excess hydroxide present in each displacement reaction. In addition, we found that sodium 4-phenylphenoxide degraded PECH to a number average molecular weight of approximately 3000, rather than strictly displacing halide as was the case with the other nucleophiles.

Table V summarizes the thermal characterization of substituted PPO, and demonstrates that although the Tg is easily dropped with any of the substitutents, liquid crystalline behavior is not observed until 4-methoxy-4'-hydroxybiphenyl is decoupled from backbone PPO by ten methylenic units. Therefore, liquid crystalline behavior can be obtained from very rigid polymers, provided a long enough spacer is employed. A smectic liquid crystalline mesophase was confirmed by polarized optical microscopy for Me10COO-PECH, but the exact smectic phase could not be determined because some thermal crosslinking takes place during extensive annealing. This could be the result of the presence of unreacted bromobenzyl groups. In contrast to Me10COO-PPO, Ph10COO-PPO is not liquid crystalline. Although there is comparatively little substitution in this case, p-biphenyl itself would not be expected to act as a mesogen in such a rigid polymer due to its low degree of anisotropy and polarizability.

Comparison of Tables V and VI demonstrates that the thermal behavior of Me10COO-PPO and Me10COO-PECH are very similiar, with the glass transition temperatures converging with substitution. Therefore, it appears that when very long spacers are used with the same mesogen, the polymer backbone has little effect on the thermotropic phases formed.

In contrast to the substituted PPO's, it is theoretically possible to obtain the same substituted PECH's by homopolymerization of the corresponding mesogenic oxirane, or by its copolymerization with epichlorohydrin. We have attempted these polymerizations in order to better interpret the thermal behavior of the more complicated copolymers that we have obtained by polymer analogous reactions. Homopolymerization would be instructive because the incorporation of nonmesogenic units into liquid crystalline homopolymers doesn't as a rule change the type of mesophase obtained (5).

However, oxiranes are generally difficult to polymerize. One possibility is cationic ring opening polymerization. This however results in high conversion to cyclic oligomers due to backbiting of the oxonium ion chain end to produce stable six-membered dioxane molecules (30). In order to obtain linear polymers, the activated monomer mechanism can be used. Because of the addition of an alcohol to the cationic system, propogation occurs by attack of a neutral growing hydroxyl terminated chain end on a protonated (i.e. activated) monomer, thereby eliminating the possibility of backbiting (30-32). However, it is usually not possible to obtain high molecular weight polymers because as the ratio of monomer to initiator increases, so does the possibility for competition by conventional cationic propagation increase. This results in both linear and cyclic oligomers. To prepare linear high polymers from oxiranes, ionic coordinative catalysts are usually employed. The Vandenberg catalyst, $R_3Al.0.6\ H_2O$, is the most frequently used coordinate catalyst (33-35). The obtained polymers are, however, highly crystalline (isotactic) and therefore difficult to characterize by techniques requiring solubility.

A fourth alternative is $AlEt_3$/metal chelate polymerizations, such as the $AlEt_3$/bis(dimethylglyoxime)nickel system. The problem with these catalysts is that they result in either high yields of low molecular weight polymers, or low yields of high molecular weight polymers, but not both high yield and high molecular weight (36,37). A more promising method allowing the control of molecular is a living polymerization initiated by metalloporphyrins. The initiator is generated by the reaction of diethylaluminum chloride and 5,10,15,20-tetraphenylporphorine, which is used either by itself (38) or in combination with a quaternized ammonium or phosphonium salt (39) to generate a single or two growing chains respectively by insertion of the monomer in the aluminum-halide bonds. So far, none of these polymerization methods could lead to a convenient method for the polymerization and copolymerization of mesogenic oxiranes. Work on this line is in progress in our laboratory.

In contrast to PPO, Table V demonstrates that no spacer is required to obtain liquid crystalline behavior from PECH. Figures 1 thru 8 show some representative DSC traces for Me10COO-PECH, Me3COO-PECH and Me4COO-PECH. In addition to the first cooling and second heating scans, the first heating scan is also shown. This is because the multiple endotherms observed with all spacers in this scan can be reproduced simply by annealing above Tg for several hours. Therefore, these endotherms cannot be dismissed as traces of solvent or the result of thermal history, and the phases are evidently kinetically controlled. It must be noted that this is the first time liquid crystalline polymers of such high molecular weight have been obtained. We have found with main-chain liquid crystalline polymers (40) that beyond a critical molecular weight, not only are the crystalline transitions kinetically controlled, but the liquid crystalline transitions also become kinetically rather than thermodynamically controlled, presumably as a result of chain entanglements. This results in a higher degree of supercooling than is normally observed for liquid crystalline phases, especially for smectic mesophases, as is seen here.

Figures 2 and 5 demonstrate that there is a minimum concentration limit necessary for mesophase formation in copolymers of mesogenic monomers with nonmesogenic monomers (3), since the liquid crystalline endotherm is not observed in the second heating scan. In addition, Figure 5 demonstrates that the first endotherm in each sample may be a crystalline melting. The first heating scan of 0.23 Me4COO-PECH shows a strong liquid crystalline endotherm at 44.7°C, and a weak endotherm in the form of a tail at the temperature corresponding to the weak melting endotherm in the second scan. This weaker first endotherm is obviously crystalline melting since cold crystallization of the same enthalpic content is required just prior to the melting. This, and the lack of a crystallization exotherm on cooling demonstrates that crystallization is slow and occurs over a large range of temperatures with these samples. This is probably due to the proximity of the Tg and the temperature of melting (Tm), combined with a great deal of crystalline supercooling. Apparently, structural ordering in these PECH systems is much easier in solution (i.e. prior to precipitation in the nonsolvent methanol) than by thermal rearrangements.

Beyond the minimum mesogenic concentration limit of approximately 26% with these shorter spacers (or no spacer), isotropization is also seen in the second heating scans with melting seen only as a tail to isotropization. Once 51% substitution is reached with Me4COO-PECH, we see in addition to melting and the "normal" liquid crystalline endotherm (Ti), crystallization followed by a second endotherm at higher temperature. However, it is not observed again on reheating scans unless the sample is annealed, and the enthalpy of the endotherm in the second heating scan is equal to the total enthalpy content of the first two peaks in the first scan. When substitution is increased further, this third endotherm is seen as a minor peak in additional heating scans and therefore represents the true isotropization temperature.

Preliminary room temperature x-ray data of 0.65 Me4COO-PECH indicates that the sample presents a highly ordered smectic mesophase which was not yet completely assigned. The textures seen by polarized optical microscopy are also typical of smectic phases. Due to the very high molecular weights involved, textures specific to mesophaes in thermodynamic equilibrium could not be developed within a reasonable amount of time by annealing.

CONCLUSIONS

These results demonstrate that side-chain liquid crystalline polymers can be synthesized by polymer analogous reactions from thereoretically any polymer backbone. When the polymer backbone is rigid, as in the case of PPO, a long spacer is required both to decrease the Tg of the parent polymer and to partially decouple the mobility of the mesogens from that of the main chain. Flexible backbones such as PECH do not require a long spacer between the mesogen and the polymer main chain. Liquid crystallinity can be induced by directly attaching the mesogen to the polymer backbone providing that the Tg of the resulting polymer is below the isotropization temperature. This can easily be accomplished with PECH copolymers where the flexible nonsubstituted structural units may behave as a spacer.

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FIGURE CAPTIONS

Scheme 1. Synthetic routes used for the modification of PPO and PECH.

Figure 1. DSC traces of 0.36 MeO-PECH (#2/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 2. DSC traces of 0.22 Me3COO-PECH (#3/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 3. DSC traces of 0.26 Me3COO-PECH (#4/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 4. DSC traces of 0.34 Me3COO-PECH (#6/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 5. DSC traces of 0.23 Me4COO-PECH (#7/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 6. DSC traces of 0.42 Me4COO-PECH (#8/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 7. DSC traces of 0.51 Me4COO-PECH (#10/Table IV): (A) first heat; (B) first cool; (C) second heat.

Figure 8. DSC traces of 0.65 Me4COO-PECH (#13/Table IV): (A) first heat; (B) first cool; (C) second heat.

Table I. Polymers with Direct Attachment of Mesogens.

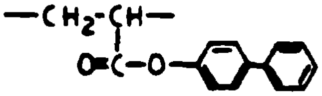
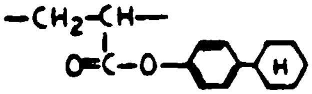
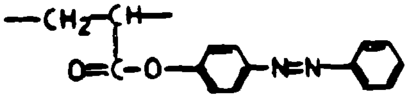
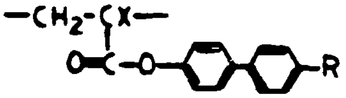
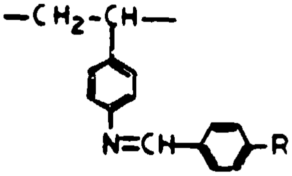
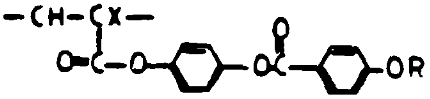
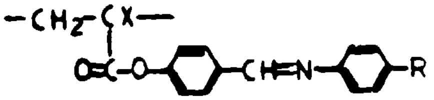
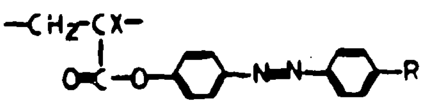
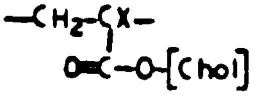
Polymer			Phase Transitions	Reference
			S 285 I	7-11
			S 205 I	7,8
			K 81 S 222 I	13
	X = H	R = CN	S 270 I	12
	X = H	R = C_5H_{11}	S 303 I	12
	X = CH_3	R = CN	S 240 I	12
	X = CH_3	R = C_5H_{11}	S 232 I	12
		R = OC_4H_9	K 88.3 N 120.6 I	13
		R = OC_6H_{13}	K 94.5 S 97.7 N 116 I	13
		R = CN	K 113.8 N 140.5 I	14
	X = H	R = $C_{16}H_{33}$	S 200 I	5
	X = CH_3	R = C_4H_9	S 270 I	5
	X = CH_3	R = C_9H_{19}	S 220 I	5
	X = CH_3	R = $C_{12}H_{25}$	S 215 I	5
	X = CH_3	R = $C_{16}H_{33}$	S 220 I	5
	X = H	R = OC_2H_5	K 78 N 136.5 I	15
	X = H	R = COOH	K 201 S 226 I	14
	X = CH_3	R = COOH	K_1 182 K_2 201 S 205 N	16
	X = CH_3	R = CH_3	S 270 I	5
	X = H	R = OC_5H_{11}	S >270 I	5
	X = CH_3	R = OC_5H_{11}	S >270 I	5
	X = H		K 125.8 I (124.8 C 91 K)	17
	X = CH_3		K 114.8 (111.8 C)	17

Table II. Influence of the Main Chain Flexibility on Liquid Crystalline Phase Transitions for Polymers with Cyano-biphenyl as Mesogen.

Mainchain	n[a]	Tg (C)	Ti (C)	Phase	Reference
Polysiloxane	6	14	166	S	18
	9	-1	157	N	19
Polyacrylate	2	50	112	N	20
	5	40	120	N	20
	6	35	125	S	18
	11	25	145	S	20
Polymethacrylate	2	95	——	—	20
	5	60	121	S	20
	6	55	100	S	18
	11	40	121	S	20

[a] length of methylenic units between mesogen and main chain

Table III. Reaction Conditions and Results of Synthesis of PPO Containing Biphenyl Groups.*

#	Nucleophile	Mole Fraction Structural Units Containing $-CH_2Br$	Moles per Mole $-CH_2Br$		Reaction		$\%CH_2Br$ Substituted
			Nucleophile	TBAH	Temp. (°C)	Time (hr)	
1	biPhO-$(CH_2)_3$COOK	0.52	2.2	0.22	25	45	25
2		0.74	1.8	0.24	25	45	26
3		0.74	1.8	0.12	60	46	100
4	MeO-biPhO-$(CH_2)_3$COOK	0.52	2.0	0.19	25	40	15
5		0.74	2.0	0.19	25	40	12
6		0.74	1.7	0.39	60	61.5	100
7	biPhO-$(CH_2)_4$COOK	0.52	2.0	0.21	25	62	87
8		0.74	1.9	0.07	25	62	93
9		0.74	1.9	0.14	60	46	100
10	MeO-biPhO-$(CH_2)_4$COOK	0.52	2.1	0.14	25	62	50
11		0.74	2.1	0.10	25	62	61
12		0.74	2.0	0.39	60	61.5	100
13	biPhO-$(CH_2)_{10}$COOK	0.52	2.0	0.12	25	96	25
14		0.74	1.9	0.21	25	96	24
15	MeO-biPhO-$(CH_2)_{10}$COOK	0.74	0.9	0.24	60	54.5	71
16		0.74	0.9	0.24	60	139.5	75

* Solvent = toluene

Table IV. Reaction Conditions and Results of Synthesis of PECH Containing Methoxybiphenyl Groups.*

#	Nucleophile	Moles per Mole $-CH_2Cl$		Reaction Time (hr)	$\%CH_2Cl$ Substituted
		Nucleophile	TBAH		
1	MeO-biPhONa	0.76	0.10	92	29
2		0.76	0.10	140	36
3	MeO-biPhO-$(CH_2)_3$COOK	0.69	0.13	91	22
4		0.75	0.12	108.5	26
5		0.75	0.12	139.5	30
6		0.75	0.12	158.5	34
7	MeO-biPhO-$(CH_2)_4$COOK	0.75	0.12	19	23
8		0.75	0.12	49	42
9		0.75	0.12	83	52
10		0.73	0.11	91	51
11		0.75	0.12	115.5	62
12		0.75	0.12	140	65
13		0.75	0.12	159.5	65
14		0.75	0.12	181.5	65
15	MeO-biPHO-$(CH_2)_{10}$COOK	0.64	0.17	54	17

* Solvent = DMF; 60°C

Table V. Thermal Characterization of PPO Containing Biphenyl Groups.

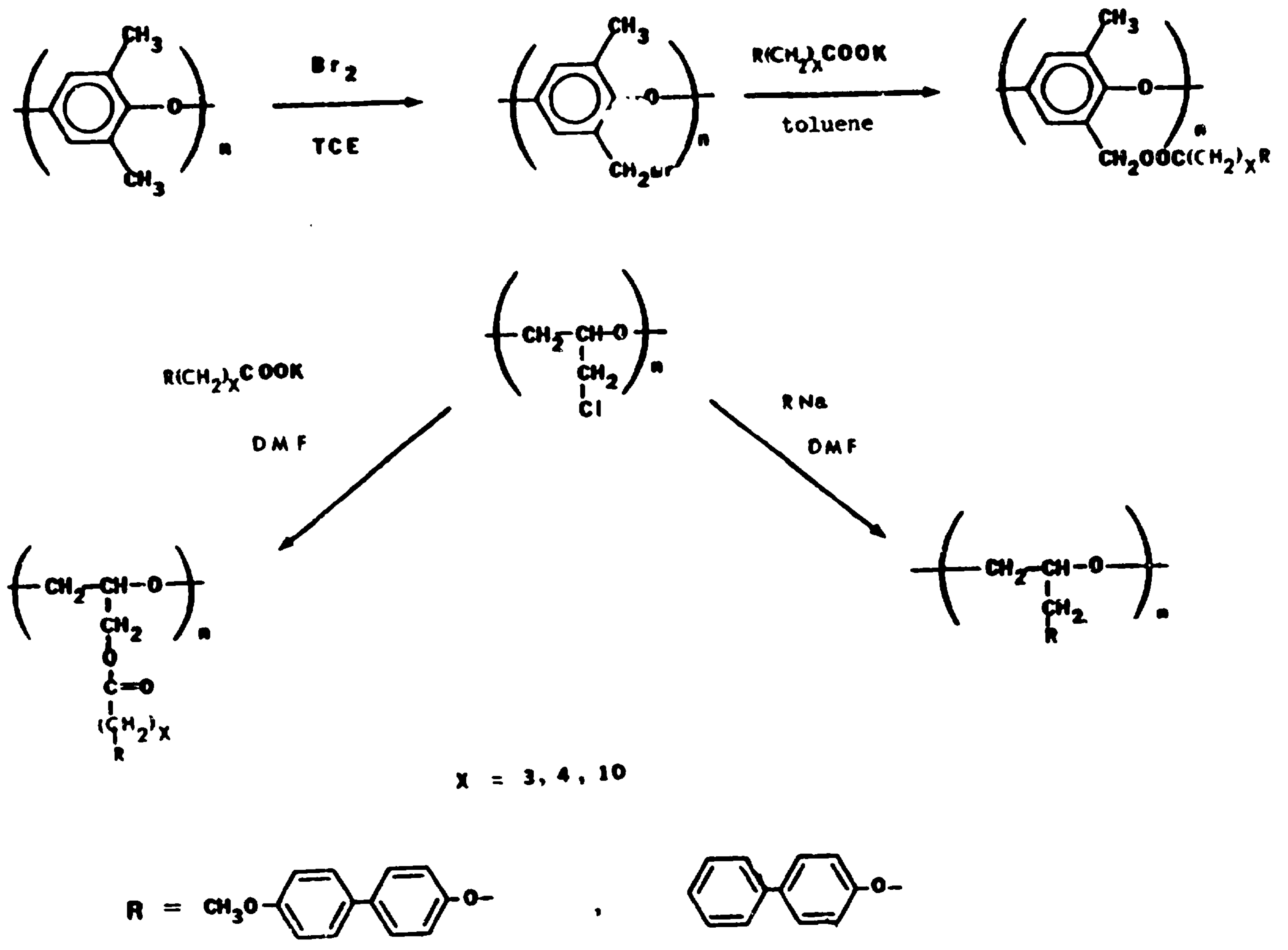
#[a]	Polymer Sample	Temperature (°C)			
		Heating		Cooling	
		Tg	Endotherms	Tg	Exotherms
1	0.13 Ph3COO-PPO[b]	141.7	—		
2	0.19 Ph3COO-PPO	130.0	—		
3	0.74 Ph3COO-PPO	69.5	—		
4	0.08 Me3COO-PPO	172.5	—		
5	0.09 Me3COO-PPO	155.2	—		
6	0.74 Me3COO-PPO	69.4	—	58.4	—
7	0.43 Ph4COO-PPO	80.8	—		
8	0.69 Ph4COO-PPO	67.0	—		
9	0.74 Ph4COO-PPO	59.6	—		
10	0.26 Me4COO-PPO	106.2	—		
11	0.45 Me4COO-PPO	89.2	—	85.6	—
12	0.74 Me4COO-PPO	62.5	—	53.1	—
13	0.13 Ph10COO-PPO	105.5	—		
14	0.18 Ph10COO-PPO	83.7	—		
15	0.53 Me10COO-PPO	54.2	114.5	39.2	77.5
16	0.56 Me10COO-PPO	38.6	72.4, 116.8, 129.0	c	40.4, 101.4

[a] from Table III; [b] mole fraction of mesogen substituted structural units; [c] buried in peak

Table VI. Thermal Characterization of PECH Containing Methoxybiphenyl Groups.

* #	Temperature (°C) 1st Heat		1st Cool		2nd Heat	
	Tg	Endotherms	Tg	Exotherms	Tg	Endotherms
1	9.2	66.6, 82.9	- 1.6	65.7	7.0	81.2
2	17.3	60.1, 80.5	- 3.9	62.9	12.4	81.6
3	-4.1	39.8, 49.6	- 9.8	——	-2.5	——
4	-0.9	7.9, 52.3	-11.7	13.9	-0.4	43.1
5	0.1	51.6, shoulder	- 7.3	26.7	1.8	51.7
6	3.7	50.0, shoulder	- 6.9	31.6	3.7	56.8
7	-9.1	shoulder, 44.7	-13.6	——	-7.5	34.1
8	7.7	55.0, 70.3	2.0	42.0, 55.2	6.2	70.7
9	18.6	58.8, 85.4, 107.2	4.7	70.6	17.3	88.1
10	17.0	57.3, 83.5, 103.2	- 5.2	65.7	16.0	83.4
11	34.3	73.5, 100.5, 114.4	——	82.9	37.6	101.7
12	35.2	72.0, 105.0, 117.3	——	89.0	40.2	107.1
13	36.0	67.0, 107.9, 119.2	——	91.4	47.7	110.4
14	34.1	62.4, 107.8, 118.1	——	91.1	44.1	109.8
15			-20.3	34.7, 88.6	-12.9	45.7, 74.1, 105.4

*from Table IV


Br2
TCE
R(CH2)xCOOK
toluene
R(CH2)xCOOK
DMF
RNa
DMF
X = 3, 4, 10
R = CH3O-

Scheme 1

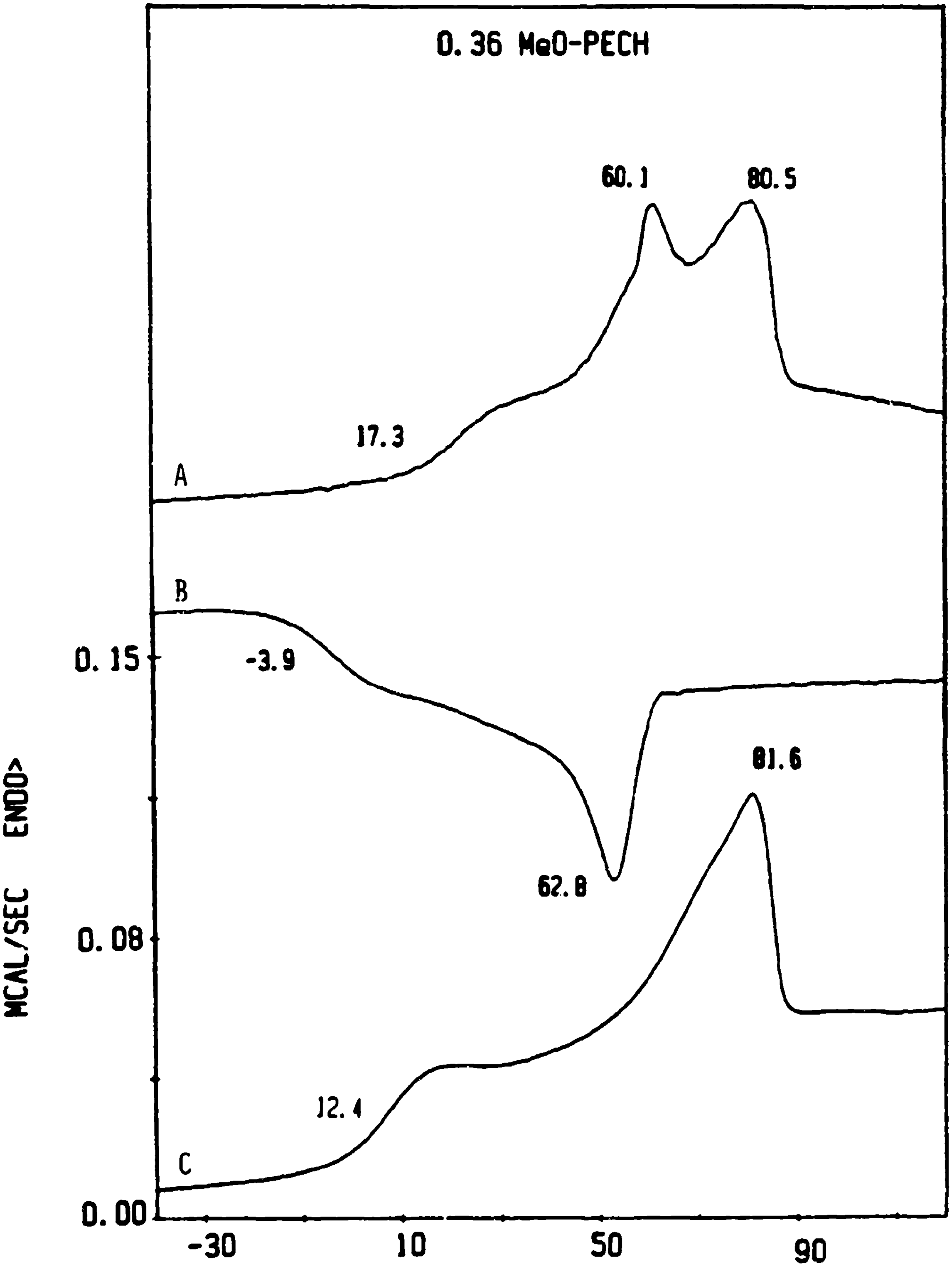

0.36 MeO-PECH
60.1
80.5
17.3
A
B
-3.9
62.8
81.6
12.4
C
0.15
0.08
0.00
MCAL/SEC ENDO>
-30
10
50
90
TEMPERATURE (C)

Fig. 1

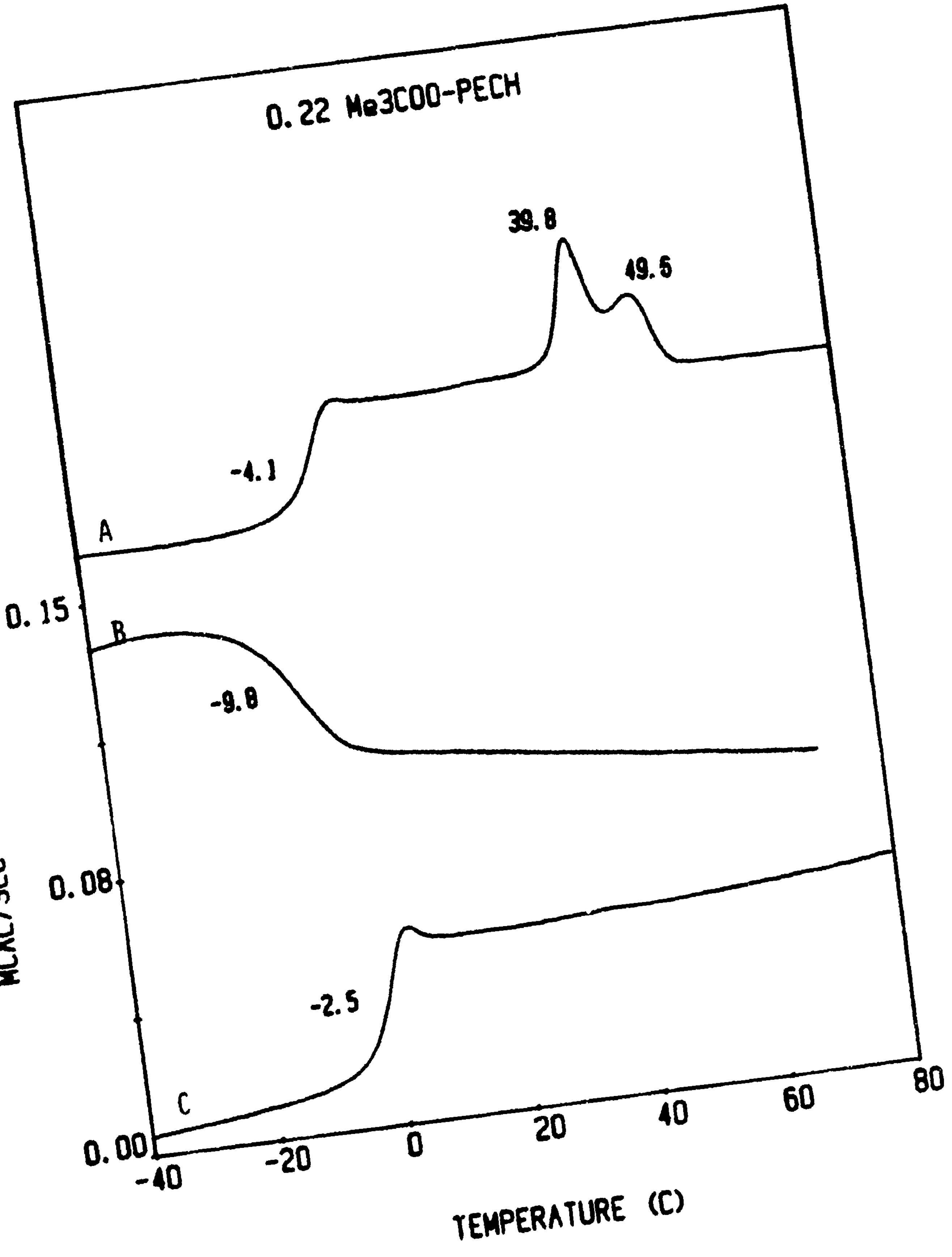

0.22 Me3COO-PECH
39.8
49.6
-4.1
A
0.15
B
-9.8
MCAL/SEC   ENDO>
0.08
-2.5
C
0.00
-40
-20
0
20
40
60
80
TEMPERATURE (C)

Fig. 2

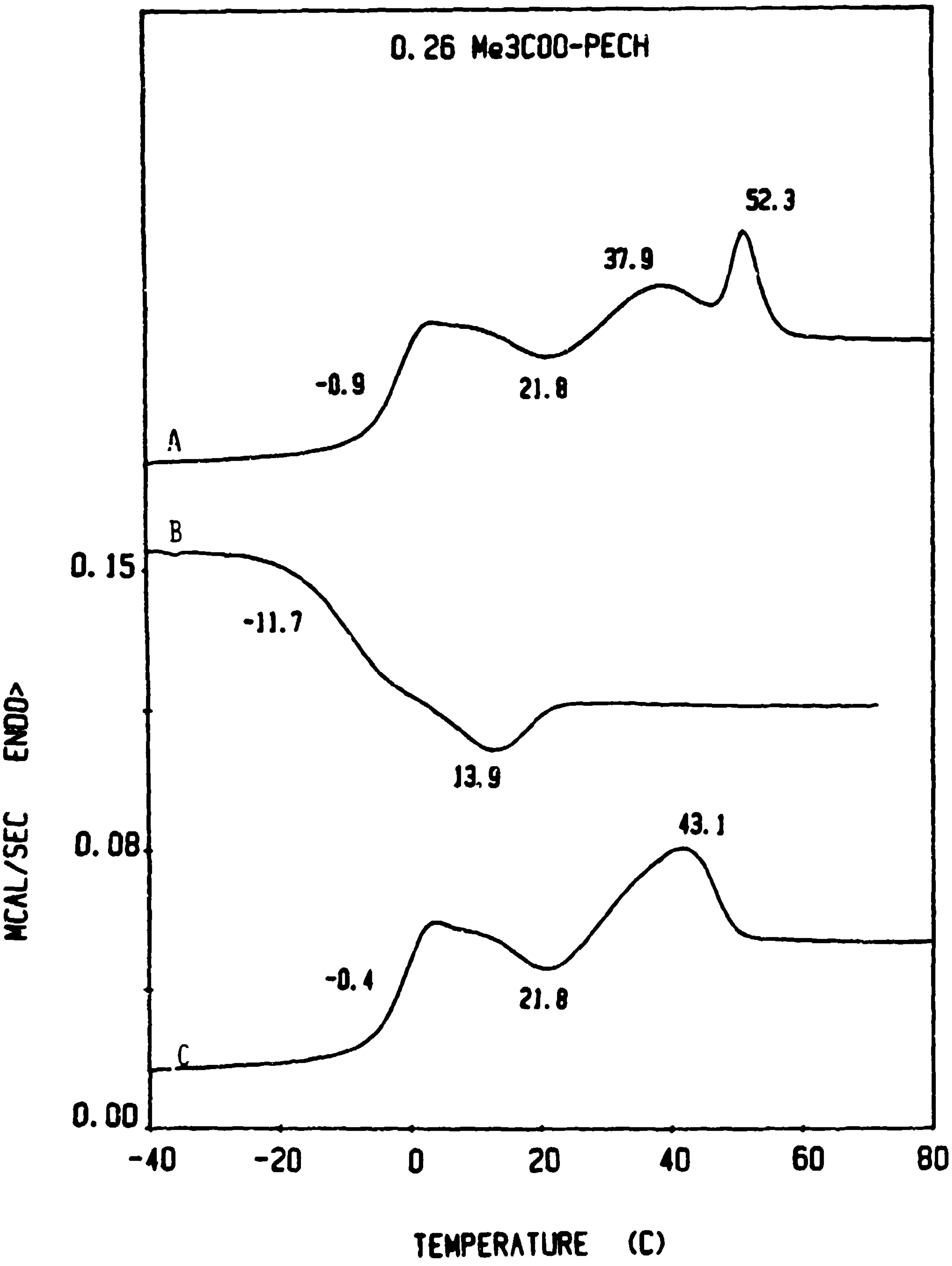

0.26 Me3COO-PECH
52.3
37.9
-0.9
21.8
A
B
-11.7
13.9
43.1
-0.4
21.8
C
0.15
0.08
0.00
MCAL/SEC ENDO>
-40
-20
0
20
40
60
80
TEMPERATURE (C)

Fig. 3

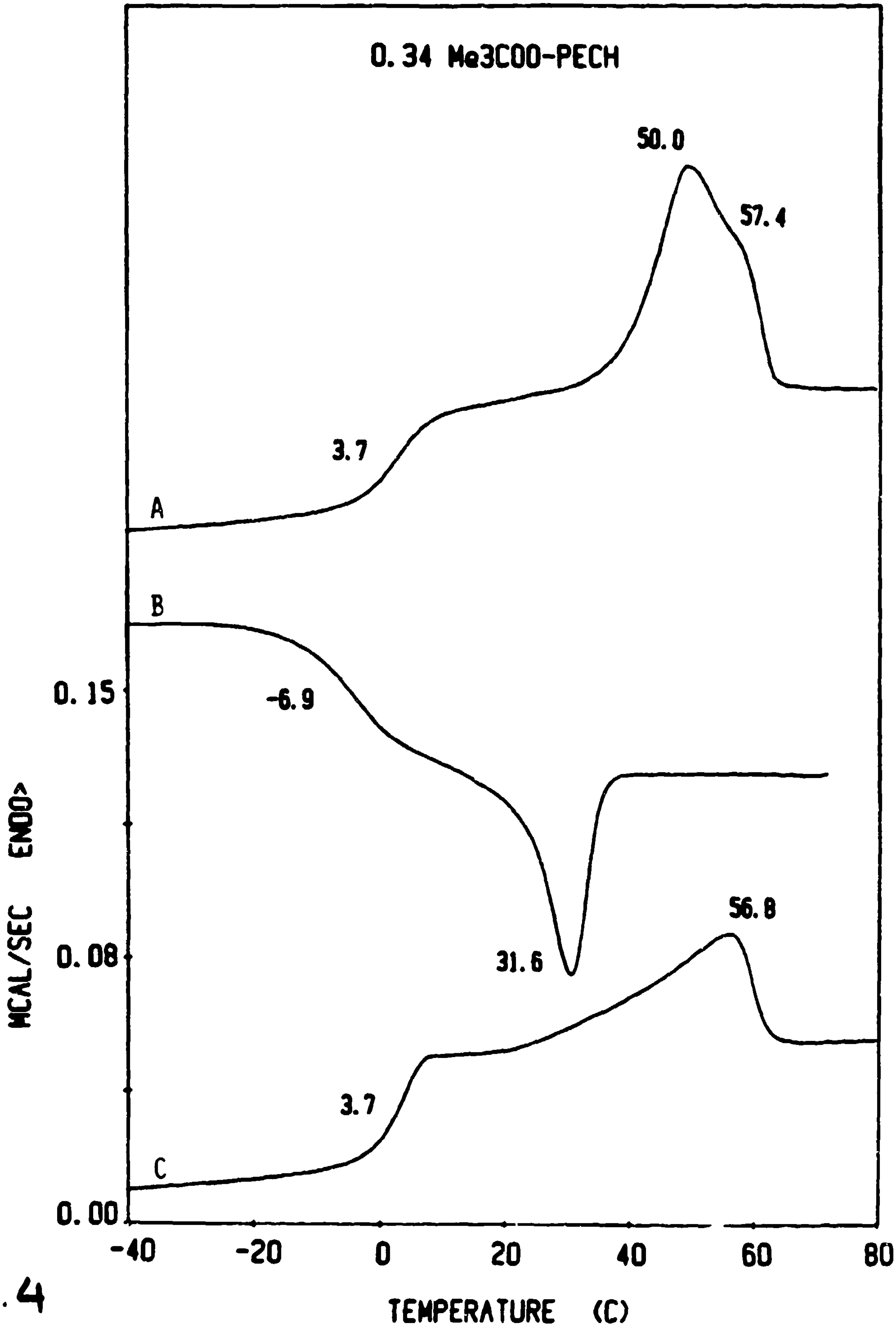

0.34 Me3COO-PECH
50.0
57.4
3.7
A
B
-6.9
31.6
56.8
3.7
C
0.15
0.08
0.00
MCAL/SEC ENDO>
-40
-20
0
20
40
60
80
TEMPERATURE (C)

Fig. 4

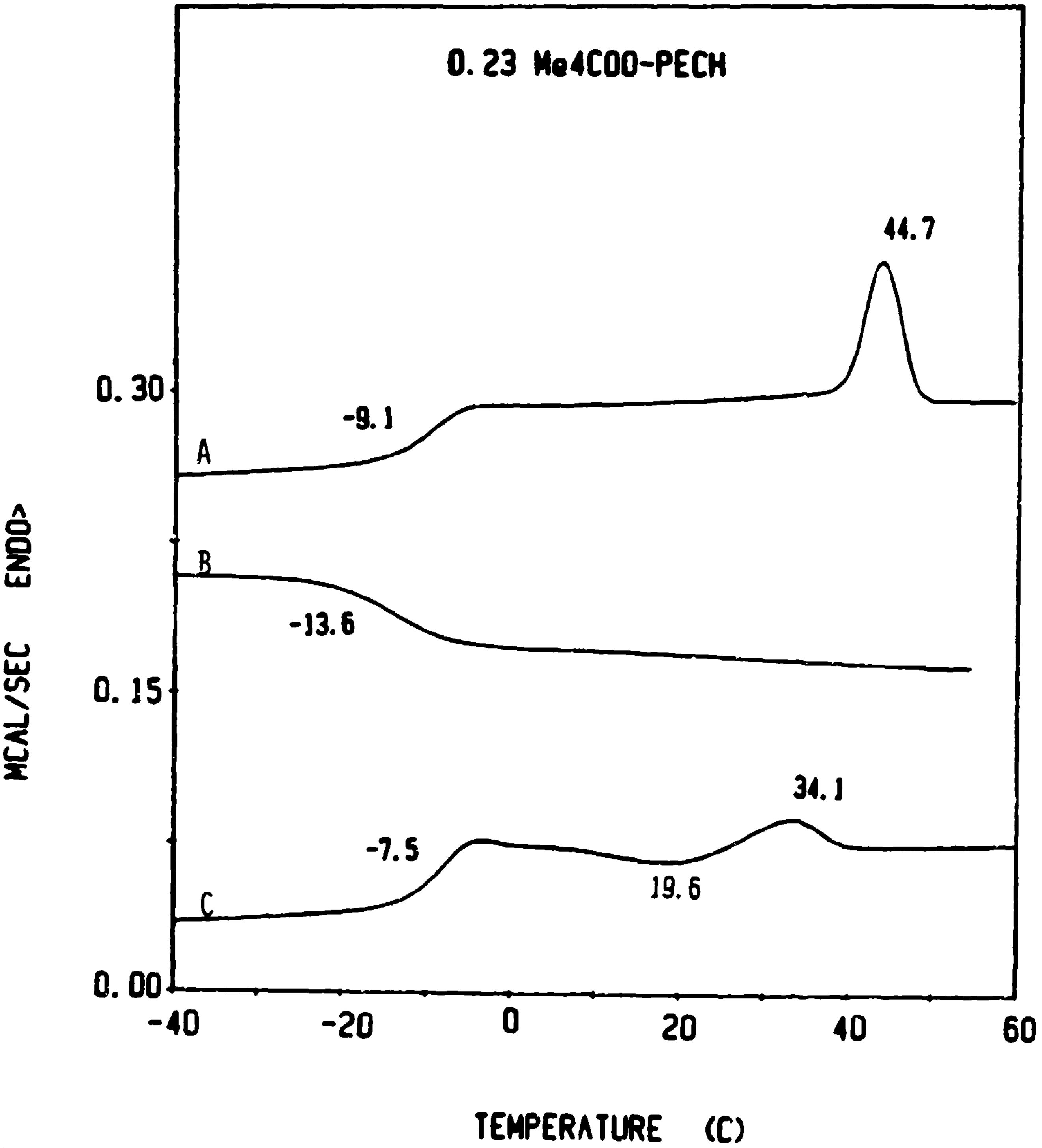

0.23 Me4COO-PECH
44.7
0.30
-9.1
A
B
-13.6
0.15
34.1
-7.5
19.6
C
0.00
-40
-20
0
20
40
60
TEMPERATURE (C)
MCAL/SEC ENDO>

Fig. 5

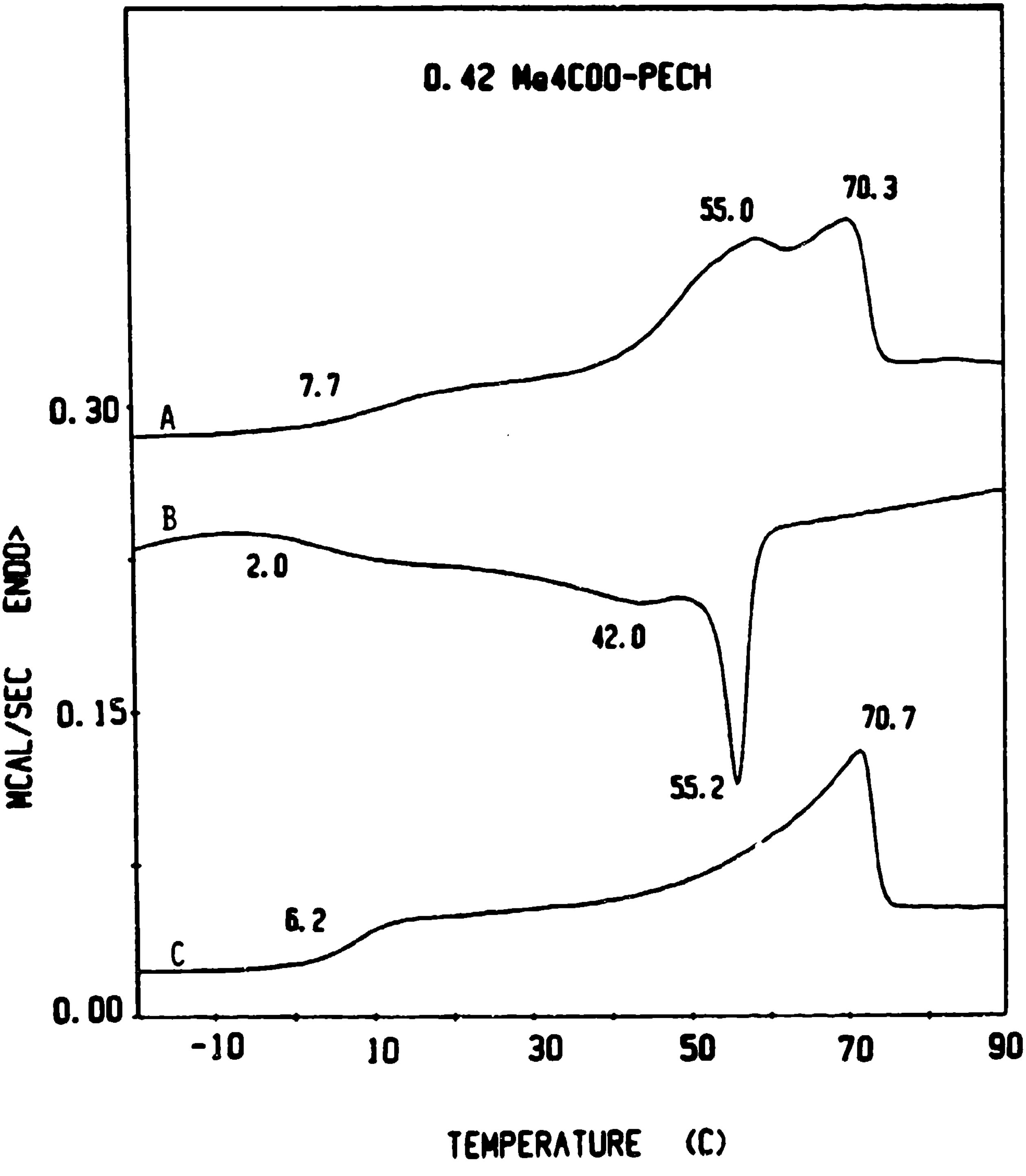

0.42 Me4COO-PECH
55.0
70.3
7.7
0.30
A
B
2.0
42.0
0.15
70.7
55.2
6.2
C
0.00
-10
10
30
50
70
90
MCAL/SEC ENDO>
TEMPERATURE (C)

Fig. 6

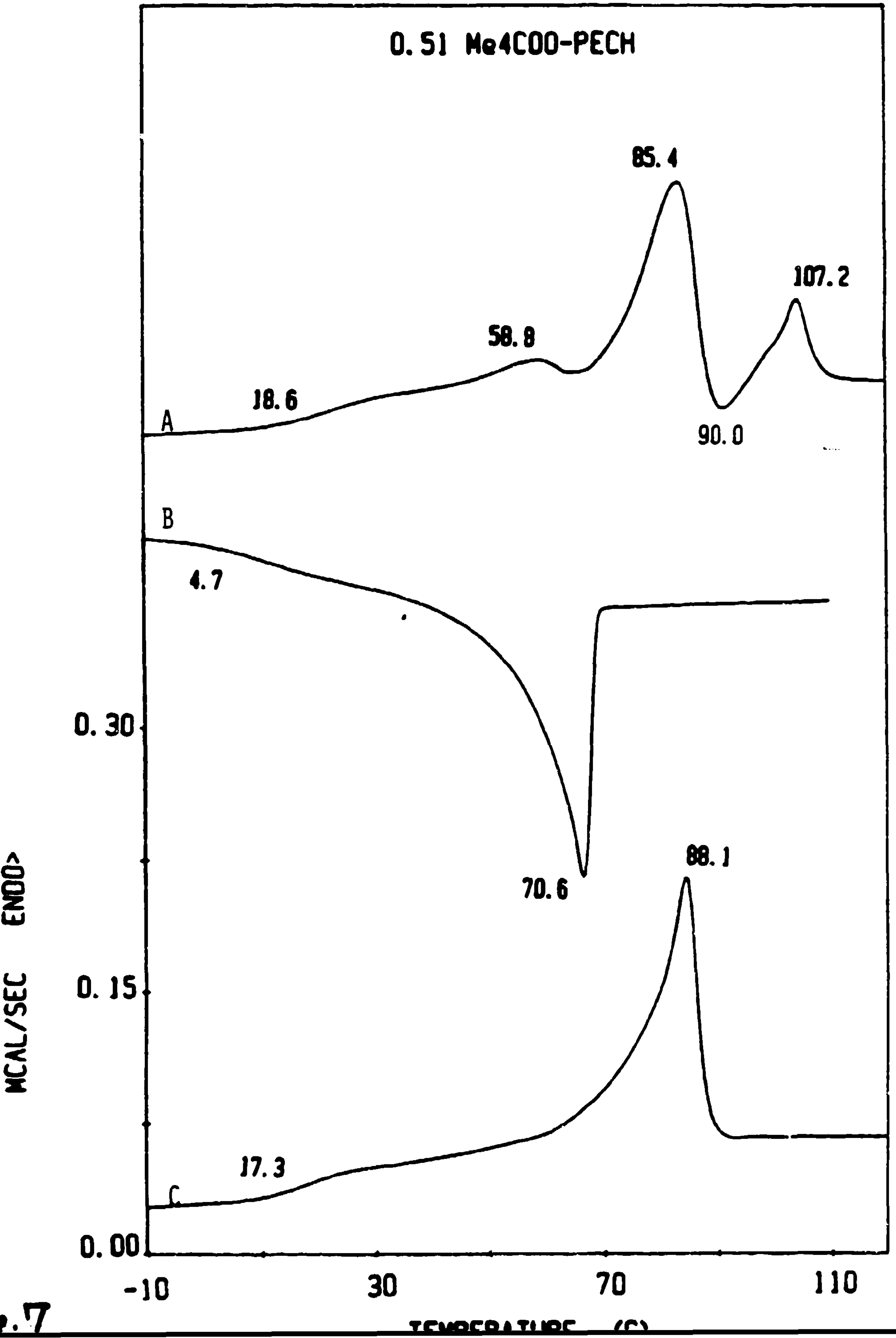

0.51 Me4COO-PECH
85.4
107.2
58.8
18.6
A
90.0
B
4.7
70.6
88.1
17.3
C
0.30
0.15
0.00
MCAL/SEC ENDO>
-10
30
70
110
TEMPERATURE (C)

Fig.7