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POROUS NETWORKS DERIVED FROM SYNTHETIC POLYMER- CLAY COMPLEXES

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POROUS NETWORKS DERIVED FROM SYNTHETIC POLYMER- CLAY COMPLEXES

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ABSTRACT

Synthetic hectorites were hydrothermally crystallized with direct incorporation of a cationic polymer poly(dimethyl diallyl ammonium chloride) (PDDA), and two neutral cellulosic polymers hydroxypropyl methylcellulose (HPMC) and hydroxyethyl cellulose (HEC). Synthetic PDDA-hectorite displays the lowest d-spacing at 15.8 Å along with less polymer incorporation (7.8 wt% organic) than the neutral polymers (18-22 wt% organic). Thermal analysis and small angle neutron scattering were used to further examine the polymer-clay systems. Clay platelets of the largest size and best stacking order occur when cationic PDDA polymer is used. PDDA also enhances these properties over the crystallites prepared for a control mineral, where no polymer is used. HEC acts to aggregate the silica, leaving less to react to form clay. The clay platelets which result from HEC are small, not stacked to a large degree, and oriented randomly. Neutral HPMC acts more like cationic PDDA in that larger clay platelets are allowed to form. The extended microstructure of the clay network remains undisturbed after polymer is removed by calcination. When no polymer is used, the synthetic hectorite has a N_2 BET surface area of 200 m^2/gm, even after calcination. This increases by 20-50% for the synthetic polymer-hectorites after the polymer is removed by calcination.

INTRODUCTION

Polymer-clay suspensions and composites have considerable importance in commercial and technological applications[1]. The fundamental chemistry of the adsorption on clays of many polymers has been well documented[2,3]. There are now new reports concerning the nature of water-soluble cellulosic polymers[1] and polyvinyl alcohol[1,4] on various clay minerals. There are also recent reports of *in situ* intercalative polymerization processes[5] to form polymer-clay composites. Tomita and co-workers have shown that layered carbons can be produced by heating polyfurfuryl alcohol or polyacrylonitrile intercalated within clays such as montmorillonite[6]. Microporous materials based on inorganic matrices and carbonized polymers have been described by Bandosz and co-workers[7]. All of these studies, however, involve modification of an existing clay mineral by such methods as ion-exchange, *in situ* intercalative polymerization, or simple adsorption of the polymer from solution. A new avenue of preparation involves the direct hydrothermal crystallization from a polymer-containing silicate gel.

We have previously reported a method for hydrothermally synthesizing hectorites with direct incorporation of organic or organometallic pillaring agents[8]. Hectorites are smectite 2:1 layered magnesium silicate clays with cation exchange properties. This general technique of direct synthesis has been used to incorporate water-soluble porphyrins and metalloporphyrins[9], phthalocyanines[10], cationic dye molecules and organometallic complexes[11], and now (see Figure 1) neutral hydroxypropyl methylcellulose (HPMC) and hydroxyethyl cellulose (HEC) polymers, and the cationic poly(dimethyl diallyl ammonium chloride) (PDDA). Neutral and cationic polymers were chosen to examine the effect of charge on crystallization and incorporation. Finally, the extended porous networks derived from removing the polymer from the inorganic matrix are probed by N_2 BET surface area and adsorption measurements, and small angle neutron scattering.

EXPERIMENTAL

Materials. Ludox HS-30, a Na^+-stabilized 30 wt% silica sol, was obtained from DuPont. Hydroxypropylmethyl cellulose (HPMC) from Dow Chemical Co., Midland, MI (Methocel 240S) had a weight average MW of 1.53×10^6. Hydroxyethyl cellulose (HEC) from Aqualon Co., Wilmington, DE (Natrosol 250 HHXR) had a viscosity average MW of 1.3×10^6. Poly(dimethyl diallyl ammonium chloride) (PDDA) was used as a 100-200K MW polycation in a 40 wt% solution of pH 5-7 (Agefloc WT40) obtained from CPS Chemical Co., Inc., Old Bridge, NJ. The water used in all experiments was both distilled and deionized.

Modification of natural clays was also carried out for comparison with the synthetic clays. SHCa-1 is a California Na^+-hectorite distributed by the Source Clays Repository, Columbia, MO. As supplied it contains approximately 50% $CaCO_3$ and iron-containing impurities that are removed by sedimentation techniques. A 1 wt% clay slurry is charged with enough polymer to cause 20 wt% organic assuming full adsorption. The slurry is stirred overnight at room temperature, then centrifuged, washed, and air-dried. In the case of PDDA the clay slurry immediately gelled and could stir only slowly. The cellulosic polymers do not dissolve in water unless a pH of 8.5-9 is initially used. Since a basic pH is detrimental to the structural integrity of clays[12], and since a SHCa slurry has a pH of 6, it was decided to not adsorb the cellulosic polymers directly onto SHCa in this work. Another natural Na^+-hectorite called Hectabrite AW, from American Colloid Co., Arlington Heights, IL, was used for the X-ray powder diffraction comparison with synthetic hectorites. Hectabrite AW was purchased in an already purified form of the natural hectorite, and has less impurities than SHCa purified in the lab.

Synthetic Hectorites. For brevity, the synthetic polymer-hectorites are referred to as synPDDA, synHEC, and synHPMC. The procedure for the hydrothermal crystallization of hectorites has been explained in detail elsewhere[8,9]. Reactants in the molar ratios of $LiF:MgO:SiO_2$ 0.266:1.00:1.52 are refluxed for 2 days as a 2 wt% aqueous slurry. This yields the ideal hectorite composition[12] $Ex_{0.66}[Li_{0.66}Mg_{5.34}Si_8O_{20}(OH)_4]$, where Ex = exchangeable monocation. The amount of polymer added was chosen such that, if all of the polymer was incorporated into the clay and assuming complete reaction, 20 wt% of the clay would be organic. Lithium (I) ions occur in the lattice as isomorphous substitutions for Mg(II), leaving a negative charge that is carried by the basal oxygen surface and compensated for by the presence of exchangeable cations and water molecules within the interlayer or gallery. In the inorganic synthetic hectorite, Li(I) is also the exchangeable cation. A certain amount of this Li(I) can be replaced by organic or organometallic cations directly from a precursor organic-containing gel. The source of MgO was freshly synthesized $Mg(OH)_2$ slurry prepared by precipitation from $MgCl_2 \cdot 6H_2O$ in dilute NH_4OH followed by numerous washings. The source of silica was Ludox HS-30. To isolate the clay, the slurry was centrifuged and washed three times or until the decant was clear, allowed to air dry, then powdered. Thin films were made by drying some of the washed slurry on a glass slide. Calcination of polymer-clays was carried out in a tube furnace using quartz boats at 400°C under air or oxygen flow for at least 4 hours.

Characterization. X-ray powder diffraction (XRD) analyses were carried out on a Scintag PAD-V instrument using Cu K_α radiation and a hyperpure germanium solid-state detector at a scan rate of 0.5° 2θ/min. The instrument was calibrated to the (101) reflection of low-quartz at 3.34 Å. Powders were either loosely packed in horizontally held trays or spread out on glass slides. Thermal gravimetric analysis (TGA) was performed either on a CAHN-121X in an oxygen atmosphere (40 ml/min) with a heating rate of 10°C/min or on a TA Instruments SDT 2960 simultaneous TGA-DTA (differential thermal analysis) under an oxygen flow of 100 ml/min. N_2 BET surface area measurements were collected on a Quantasorb Jr. sorption analyzer after outgassing at room temperature under nitrogen flow overnight. Measurements were also made on a

Autosorb-6 to obtain more detailed nitrogen adsorption/desorption behavior. SANS measurements were made at the Intense Pulsed Neutron Source at Argonne National Laboratory, Ill. Experimental conditions are published elsewhere (Carrado *et al* 1991). The powders were held in 1mm quartz cells.

RESULTS

The X-ray diffraction patterns of natural and synthetic hectorites are compared in Figure 2. SynLi, the synthetic hectorite with Li(I) exchangeable cations (no polymer), displays a pattern typical of the synthetic hectorites. This clay has a basal or d(001) spacing of 14.3 Å (6.18° 2θ). This value includes the thickness of the clay layer which is 9.6 Å for a typical smectite[12]. The peaks at 4.30 Å (20.5° 2θ) and 2.56 Å (35.6° 2θ) represent the (110,020) and (130) reflections of clay, respectively. Note that there is no sign of unreacted $Mg(OH)_2$, which would display peaks at 4.77 Å (18.6° 2θ) and 2.37Å (38.0° 2θ) for the (001) and (101) reflections of the magnesium hydroxide mineral brucite. The XRD pattern for the natural hectorite demonstrates the similarity in peak widths and intensities of hk reflections for both natural and synthetic minerals. This natural hectorite, even though extensively purified, still contains some $(Mg,Fe)SiO_3$ as indicated by the asterisks. Figure 2 also contains the XRD pattern of synPDDA; note the typical hk clay reflections. The patterns for synHPMC and synHEC were similar, except for variations in the (001) basal reflection.

The d(001) spacings, the amount of intercalant incorporated, surface areas before and after calcination, and pore volumes are listed in Table I. The polymer loadings were calculated from the wt%C and the known molecular formulas[13]. The loadings were also verified by TGA results. The C/N ratio for PDDA determined by microanalysis matches the calculated value. An energy dispersive X-ray analysis (EDX) of synPDDA did not show the presence of any chloride down to this technique's level of detection. Since most if not all the chloride from the original polycation salt is gone, only clay is responsible for compensating the PDDA charge. The elements observed were Si, Mg, O, C, N, and Li.

A comparison of the synthetic polymer-containing hectorites versus modified natural hectorites was also carried out for PDDA. The basal spacings were identical at 15.8 Å, and polymer loadings were nearly identical for the natural and synthetic clays at 5.3 wt% and 7.8 wt% organic, respectively. An EDX analysis of a natural PDDA-hectorite showed the presence of Si, Mg, O, C, F, Cl, and Fe. The level of chloride was very low however at only 0.10 wt%, showing that virtually all the chloride from PDDA has been exchanged for clay.

Nitrogen pore volume adsorption data is provided in Table I for the calcined samples. The pore size distribution of calcined synPDDA shows a large percentage at about 78 Å radius (Figure 3). This is in contrast to the synthetic cellulose hectorites, which display a simple and smooth distribution of pore sizes, also shown in Figure 3 for synHPMC.

The thermal decomposition data of polymers in their pure form and in clay composites is presented in Table II. TGA data for pure PDDA is not reported because it is a liquid. Only the weight loss regions due to organic are tabulated for the polymer-clays. Figure 4 compares the weight loss of the synthetic cellulose-hectorites to the pure celluloses. The weight loss from 25-150°C for clays is due to surface and interlayer water. The final phase of decomposition of HEC at the exceptionally high temperature of 629°C is reproducible, and not observed for HPMC.

Small angle neutron scattering (SANS) can provide information on the size, shape, and interaction of particles in a size range of 10-1000Å. It also provides information about such properties as the thickness of the clay layers, the relative size of the platelets, correlations between the platelets in terms of their packing, etc. This technique can probe the interaction of polymers with other reactants such as silica, as well as within the final product. SANS data for synthetic hectorites with Li^+, PDDA, HEC, and HPMC are shown in Figure 5. All curves merge together in the high q region, implying similar structures at smaller length scales, which approach the range accessible to conventional XRD. Data in the low q region exhibit significant differences, however, and this reflects differences in their packing densities and other interactions. The power law dependence of scattering intensity ($I = q^{-n}$), which is the slope of the linear region, is provided in Table III. The mid-q region "hump" at about $q = 0.032Å^{-1}$ is due to aggregated unreacted silica particles with a size of about 200Å.

The scattering obtained for the calcined versions of these samples after burning out of the polymer are shown in Figure 6. The power law slopes in the low-q regions do not differ significantly from the uncalcined samples. Figure 6 also contains the SANS of a natural hectorite (not calcined) for comparison. Error bars are not drawn on any of the scattering plots because, except at very high q-values, they were of smaller or comparable size to that of the data points.

DISCUSSION

Synthetic PDDA-Hectorite. Synthetic PDDA-hectorite has the smallest basal spacing of the group at 15.8 Å, which is very similar to that of pure synthetic Li^+-hectorite at 16.0 Å. This is likely a result of the charge-compensating electrostatic interaction between the negatively charged smectite layer and the positively charged nitrogens along the PDDA polymer chain coiled between the clay sheets. This charge compensation is borne out in the SEM-EDX results, in which no chloride was observed. It also explains why much less PDDA is incorporated into hectorite (7.8 wt% organic) than is the case for the other synthetic hectorites containing neutral polymers (18-22 wt% organic). PDDA can be incorporated only until the cation exchange capacity is filled, and in fact even less than this is taken up because cation size is also a factor. Specifically, PDDA has an average MW of 100-200K and a monomer repeat unit of 162 g/mol, yielding 600-1200 repeat units in one polymer chain, and therefore 600-1200 positive charges. The cation exchange capacity (c.e.c.) of a typical, ideal hectorite[12] is about 80 meq/100gm, which corresponds to a full capacity uptake level for a PDDA-clay of about 13 wt% organic[14]. Therefore, of the available c.e.c. in the synthetic mineral, about 60% can be accounted for by the PDDA with the remainder probably belonging to lithium ions.

The data from Table II show that the natural hectorite ion-exchanged with PDDA has similar basal spacings and polymer uptake as the synthetic sample. The adsorption of polycations onto smectite clays generally leads to a two-dimensional collapse of the polycation chain onto the surface with relatively short loops in the chain[2a]. Organic compounds have been reported as promoters for the crystallization of metal silicate hydrates of the magadiite type[15], and PDDA has been shown to act as a template for the formation of a new metal silicate hydrate in the same way as is known for high silica zeolites[15]. PDDA now appears to act in a similar fashion for the crystallization of smectite minerals.

For synPDDA, the SANS power law dependence of scattering intensity $I = q^{-2.02}$ indicates that the hectorite particles are large (large aspect ratio) and stacked in a layered arrangement. The smaller power law exponents for synLi and synHEC indicate smaller sizes and aspect ratios with a more random orientation. Log(I) vs. log(q) plots for the calcined synthetic hectorites are shown in Figure 6. This provides information regarding the actual clay microstructure because interactions due to polymer are removed. The scattering intensities in the mid-to-high q region for the samples prepared using neutral polymers (HEC and HPMC) are similar, indicating a similar microstructure, with power law slopes in the region of -2.5 to -2.7±0.02. A dramatic difference is seen for synPDDA with a power law slope of -3.04±0.02 in the mid-to-high q region. All of these values are closer to the exponent of -3 seen for a natural clay (Figure 6), with synPDDA looking nearly identical. In terms of successful crystallization, a large polycation appears to be more effective than either Li(I) ions or a neutral polymer.

Synthetic Cellulose-Hectorites. Synthetic HPMC-hectorite has the largest basal spacing of the synthetic polymer-hectorites at 25.2 Å (see Table I). HEC differs from HPMC in structure by primarily just one -CH_2- unit in the side chain, and yet synthetic HEC-hectorite does not display the outstanding basal spacing. In addition, their surface areas differ by a factor of two. The behavior of these two cellulosic solutions in the sol-gel preparation is probably different, because the physical properties of the final products are so dramatically affected. The difference is also evident in the SANS data. SANS of synthetic hectorites with the two cellulosic polymers (Figure 5) exhibit drastically different behavior from each other, in keeping with the differences observed in XRD and other properties. The power law exponent for synHEC is -1.40 versus -2.48 for synHPMC. The low power law exponent for synHEC indicates smaller and more randomly oriented clay layers. This is similar to results reported for synthetic hectorites crystallized in the presence of polyvinyl alcohol[16]. The larger power law exponent for synHPMC compared to synPDDA indicates even larger clay layer particles. However, the linear range of the slope for synPDDA extends over a much wide q-range, indicating ultimately a better sample.

Theng has discussed the general adsorption properties of various uncharged polysaccharides on natural clays, including cellulosic polymers, as a function of several variables[2b]. The general observation is that the adsorption of uncharged polymers increases with molecular weight unless factors such as polymer conformation, flexibility, and solubility intervene. Theng also remarks that ion-dipole interactions, which are predominant in clay adsorption of small hydroxylated organics, play only a minor role in the uptake of neutral polymers containing polar hydroxy groups[2b]. Our studies with synthetic clays conform to these observations.

Other studies concerning the adsorption of HEC and HPMC onto the swelling clay montmorillonite (an aluminosilicate isostructural with hectorite) report only the uptake level and adsorption isotherms but no XRD results[1]. These workers found that at a solution level of 3000 ppm HPMC, montmorillonite adsorbed only about 8 gm/100 gm clay[1]. The results of direct hydrothermal crystallization reported here indicate that much higher degrees of cellulose polymer loading occur; at a level of 2000 ppm, (0.2 gm/100 ml), fully 20 gm organic/100 gm clay is adsorbed. The amount of polymer adsorbed onto montmorillonite[1] decreased in the order HPMC > HEC, as occured for our synthetic hectorites.

The surface area of synLi is fairly high at 200 m^2/gm, indicating that the particle size is small[10]. It is apparent from Table I that the presence of the polymers does not lead to complete "stuffing" of the available microporous area. Removal of the polymer by calcination restores all of the original surface area. The percentage of carbon remaining after calcination is on the order of only 0.15%, and the d-spacing decreases to about 11 Å. SANS can yield complementary information to surface area measurements. For example, synHEC shows a fairly low surface area of about 70 m^2/gm, but it is not possible from this macroscopic technique to ascertain whether HEC fills the galleries or if an HEC gel acts to plug them. SANS can discriminate between these two scenarios because of its sensitivity to any modifications in the microstructure of the network, such as before and after calcination. The surface area of synHEC is restored to values similar to that of synLi upon calcination.

It is possible that HEC, in addition to being incorporated into the clay interlayers, also acts to partly coat the clay particles. This behavior would be similar to the effects of polyvinyl alcohol[16]. In synPVAs, the clay crystallites are very small and randomly oriented because PVA coats the particles just as they begin to form, precluding further growth[16]. In addition, the "hump" in Figures 5 and 6 corresponding to aggregated silica is highly pronounced for synHEC. Thus much of the silica starting material is tied up and unavailable for reaction to form clay.

SANS studies were carried out on the calcined powder samples in order to gain information on the interaction of the polymers and their disposition in the synthetic clays. The small variations in the power law slopes of synthetic polymer-clays from uncalcined to calcined indicate that the extended clay networks are similar and have not been disrupted upon calcination.

CONCLUSIONS

Most of the synthetic hectorite preparations cause extremely small crystallites to form. Because of their low aspect ratio, it is no surprise that SANS data show that they are not well stacked, even given that enough order is maintained to give a basal spacing in XRD. The larger that the platelets are allowed to grow in the x-y direction, the greater the degree of layering in the z direction. This is most evident in the case for synPDDA. A polycation therefore appears to enhance hydrothermal crystallization of hectorite over Li(I) ions or neutral polymers. Addition of other cationic species to the gel often enhances the growth of the clay crystallites[10,11]. SANS also reveals that the polymers can act to aggregate the silica, especially in the case of HEC, therefore tying up one of the essential reactants. The feasibility of direct hydrothermal crystallization for the preparation of polymer-layer silicates is demonstrated. This new technique offers the possibility of making materials not possible by modification of existing clay minerals by such methods as ion-exchange, adsorption, or polymerization of intercalated monomers.

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13. The PDDA cation is 76 wt% carbon, HPMC is 55.6 wt% C, and HEC is 51.7 wt% C.

14. Calculated as follows: (80 meq PDDA/100 gm clay) x (1 eq/1000 meq) x (1 mol/620 eq PDDA) x (100,000 gm/mol PDDA) = 13.3 g PDDA/100 gm clay; 100,000 gm/mol polymer / 161.5 g/mol monomer = 620 gm PDDA.

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Table I. Physical Properties of Synthetic Polymer-Containing Hectorites.

Gallery Species	**XRD d(001) Å**	**wt% organic**[1]	**S. A. (m^2/gm)**[2] **as prepared**	**S.A. (m^2/gm)**[2] **after calcination**	**Pore Volume (cc/gm)**[3] **after calcination**
Li (no polymer)	16.5	-	200	196	-
PDDA	15.8	7.8	207	246	1.93
HEC	19.6	17.8	69	245	2.09
HPMC	25.2	22.1	124	302	0.41

[1] calculated from %C microanalysis and known molecular formulas.

[2] N_2 BET surface areas measured before and after heating at 400°C for 4 hrs in oxygen.

[3] total nitrogen pore volume for pores less than 170 nm at $P/P_o = 0.995$.

Table II. Thermal Gravimetric Analysis (TGA) Data[1].

SAMPLE	weight loss region I temp °C	weight loss region I wt%	weight loss region II temp °C	weight loss region II wt%	ratio of wt% I/II
HEC	234	71.4	629	11.7	6.1
syn. HEC-hectorite	268	13.6	430	4.0	3.4
HPMC	228, 270	75.0	418, 475	19.6	3.8
syn. HPMC-hectorite	238	17.2	435	5.6	3.1
PDDA[2]	-	-	-	-	-
syn. PDDA-hectorite	325	4.8	505	3.3	1.4
nat. PDDA-hectorite	397	3.6	broad	2.0	1.8

[1] Data is for the regions due to decomposition of organic only.

[2] liquid.

Table III. Small Angle Neutron Scattering Data.

Sample	**Power Law Slope in Low-q Region**
synLi	-1.67 ± .027
synPDDA	-2.02 ± .005
synHEC	-1.40 ± .08
synHPMC	-2.48 ± .035
natural hectorite	-2.96 ± .003

FIGURE CAPTIONS

1. Structures of the cationic and neutral polymers used in this study: PDDA = poly(dimethyl diallyl ammonium chloride), HPMC = hydroxypropyl methyl cellulose, and HEC = hydroxyethyl cellulose.

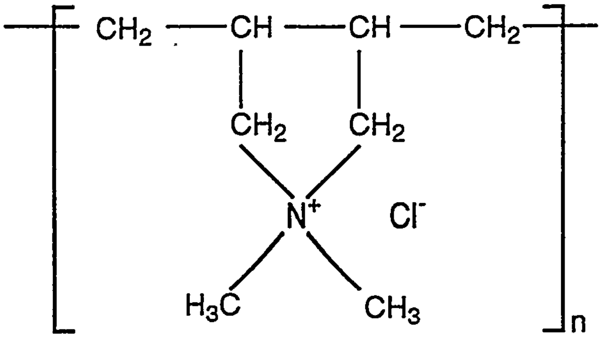
2. X-ray diffraction powder patterns of (a) a natural Na-hectorite; the peaks indicated with an asterisk (*) in the natural hectorite plot are due to (Mg,Fe)SiO3 (JCPDS file#19-605), (b) a synthetic hectorite containing Li(I) as the exchangeable cations, and (c) synthetic PDDA-hectorite.

3. Pore size distribution of the porous clay networks left after calcination of synthetic PDDA-hectorite (—•—) and synthetic HPMC-hectorite (—□—).

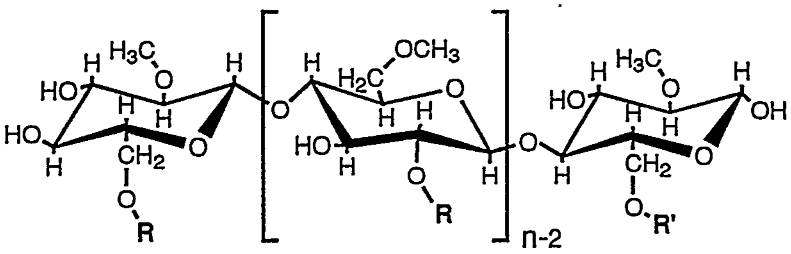
4. Thermal gravimetric analysis curves for cellulose polymers, both pure and in synthetic hectorites as incidated: (-----) weight% (——) derivative.

5. Log *I* vs. log *q* plots of the small angle neutron scattering for synthetic hectorite powders containing: (□) PDDA; (■) HPMC; (o) HEC; (•) Li. Error bars are not shown because up to q = 0.1 $Å^{-1}$ they are smaller or of comparable size to the data points. Slopes of the linear regions are provided in Table III.

6. Log *I* vs. log *q* plots of the small angle neutron scattering for calclined synthetic hectorite powders containing: (□) PDDA; (■) HPMC; (o) HEC and (•) pure natural hectorite (not calcined). Slopes of the linear regions at low q are similar to the uncalcined materials in Figure 5. Error bars are not shown because up to q = 0.1 $Å^{-1}$ they are smaller or of comparable size to the data points.



PDDA



HPMC: R = $CH_2CH(OH)CH_3$
R' = CH_3

HEC: R = $CH(OH)CH_3$
R' = H

Fig. 1

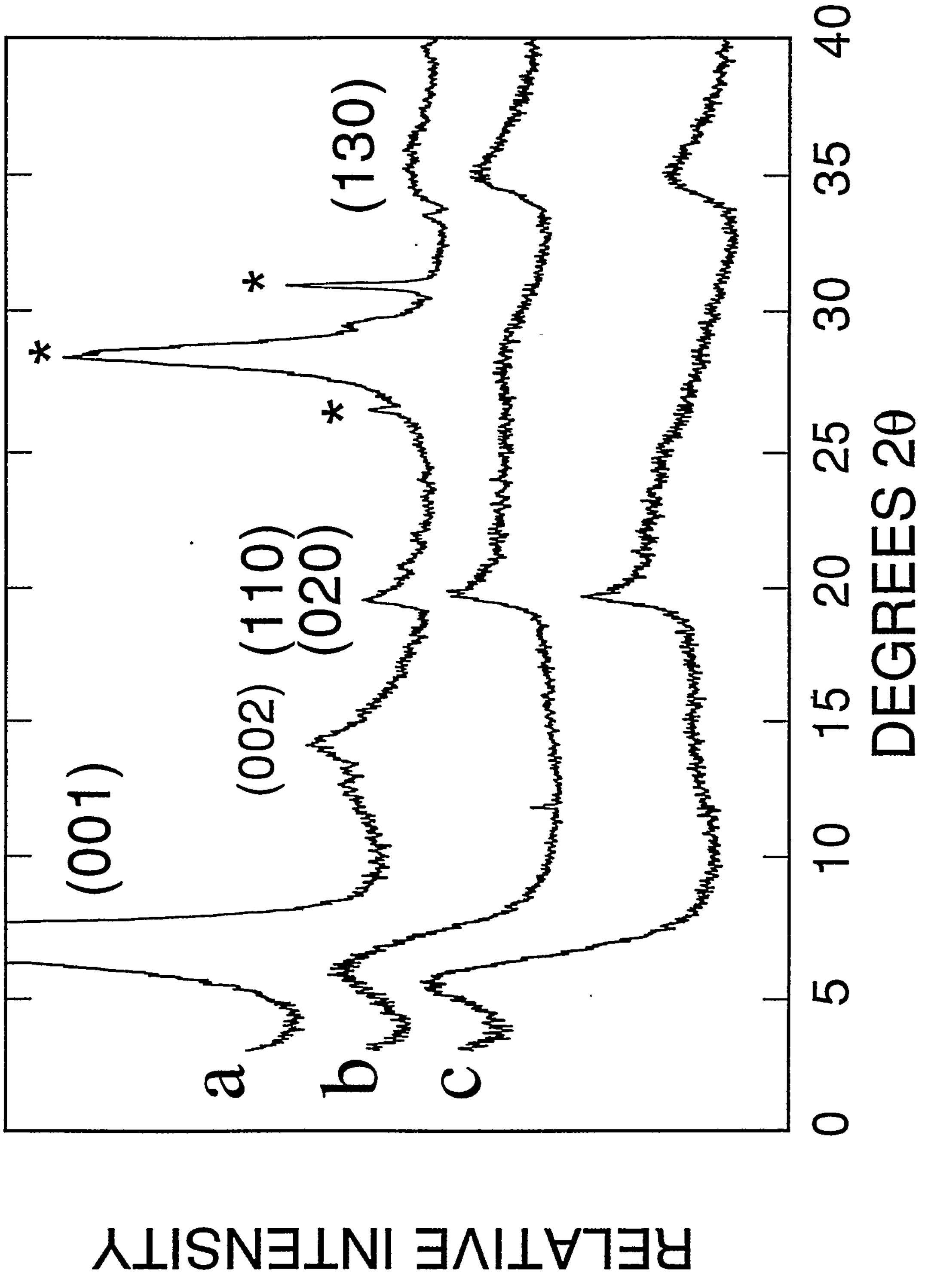

RELATIVE INTENSITY
DEGREES 2θ
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Fig. 2

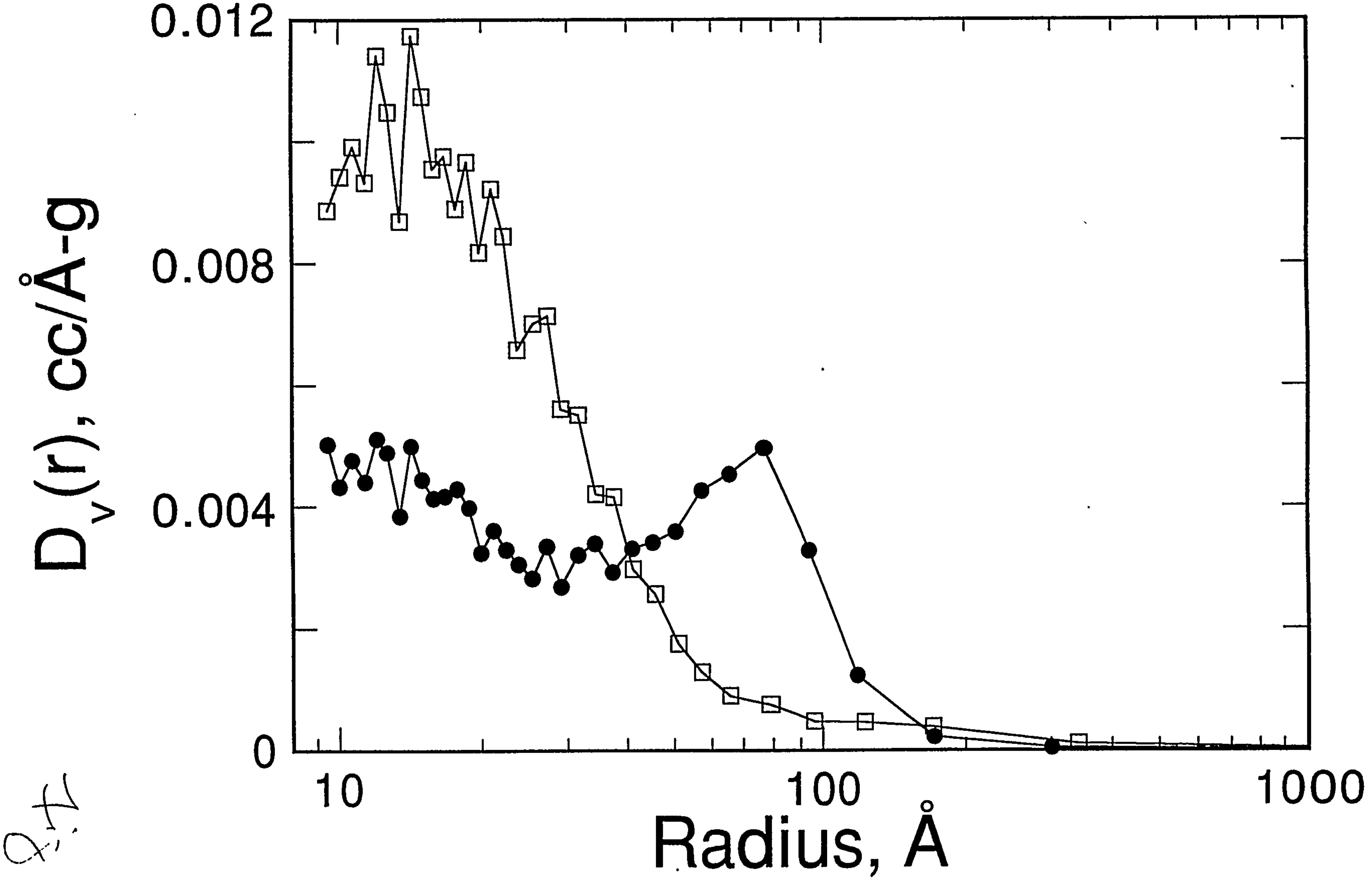

Fig 3

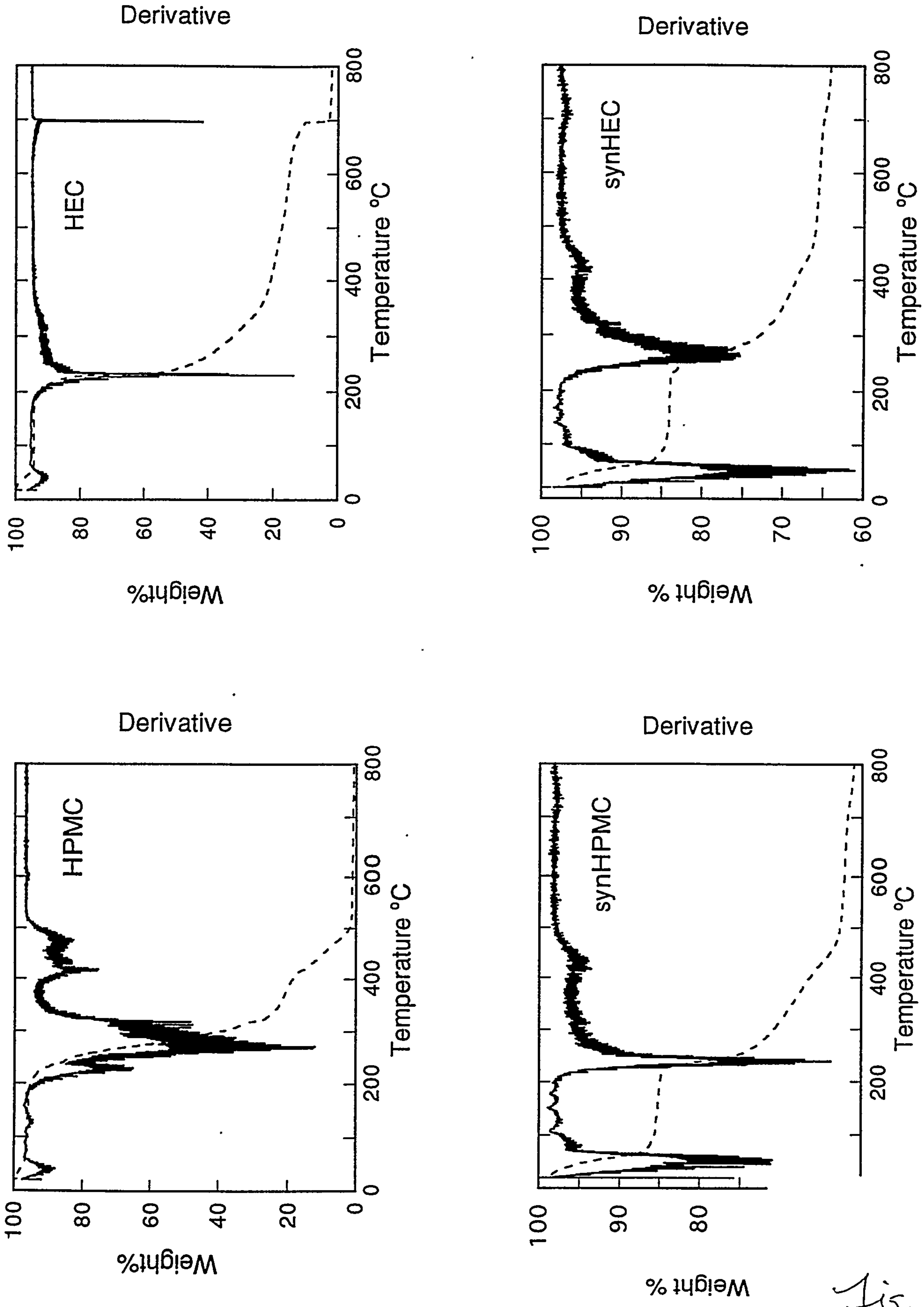
Derivative
HEC
Weight%
100
80
60
40
20
0
0
200
400
600
800
Temperature °C
Derivative
synHEC
Weight %
100
90
80
70
60
0
200
400
600
800
Temperature °C
Derivative
HPMC
Weight%
100
80
60
40
20
0
0
200
400
600
800
Temperature °C
Derivative
synHPMC
Weight %
100
90
80
200
400
600
800
Temperature °C

Fig 4

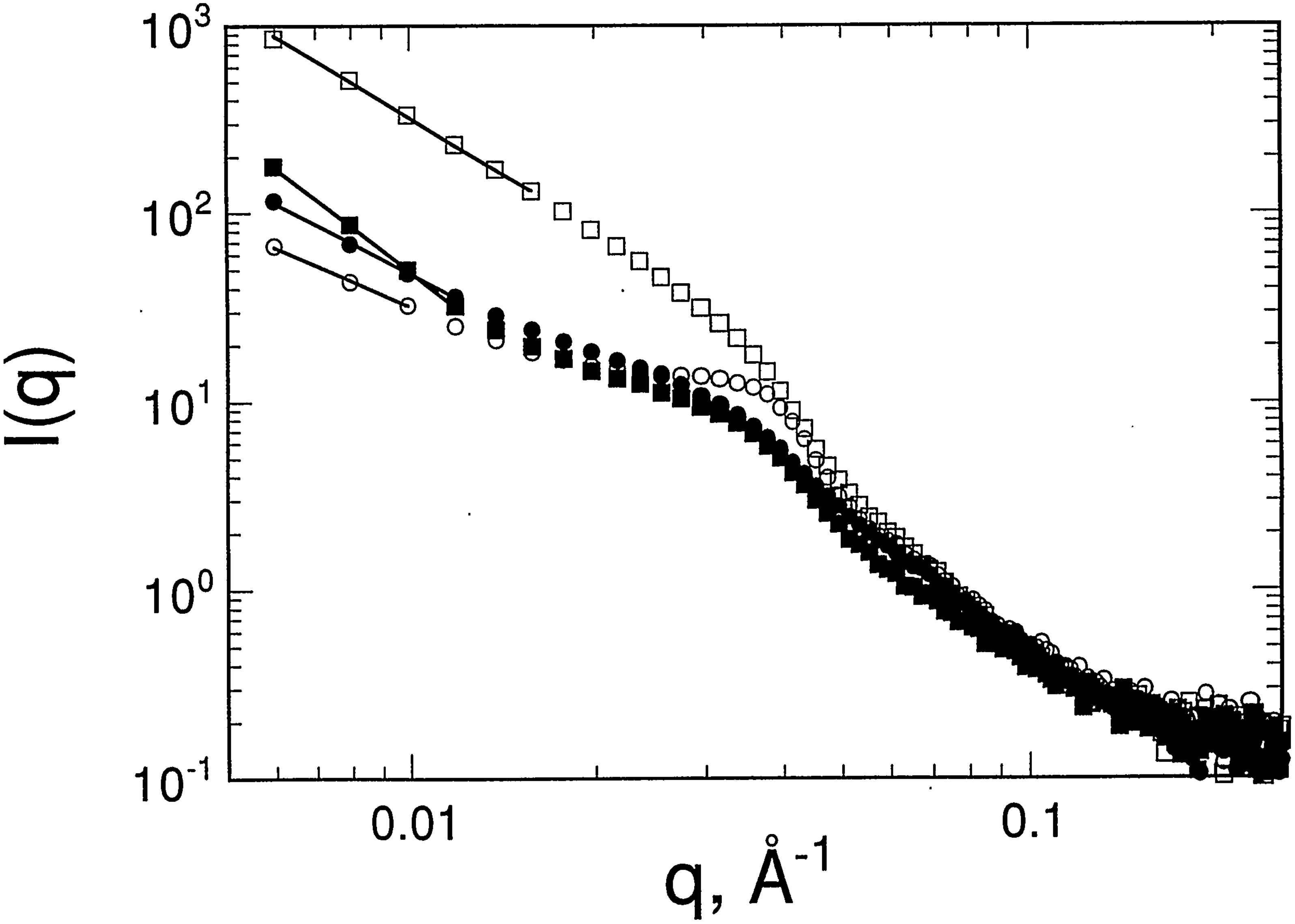

Fig. 5

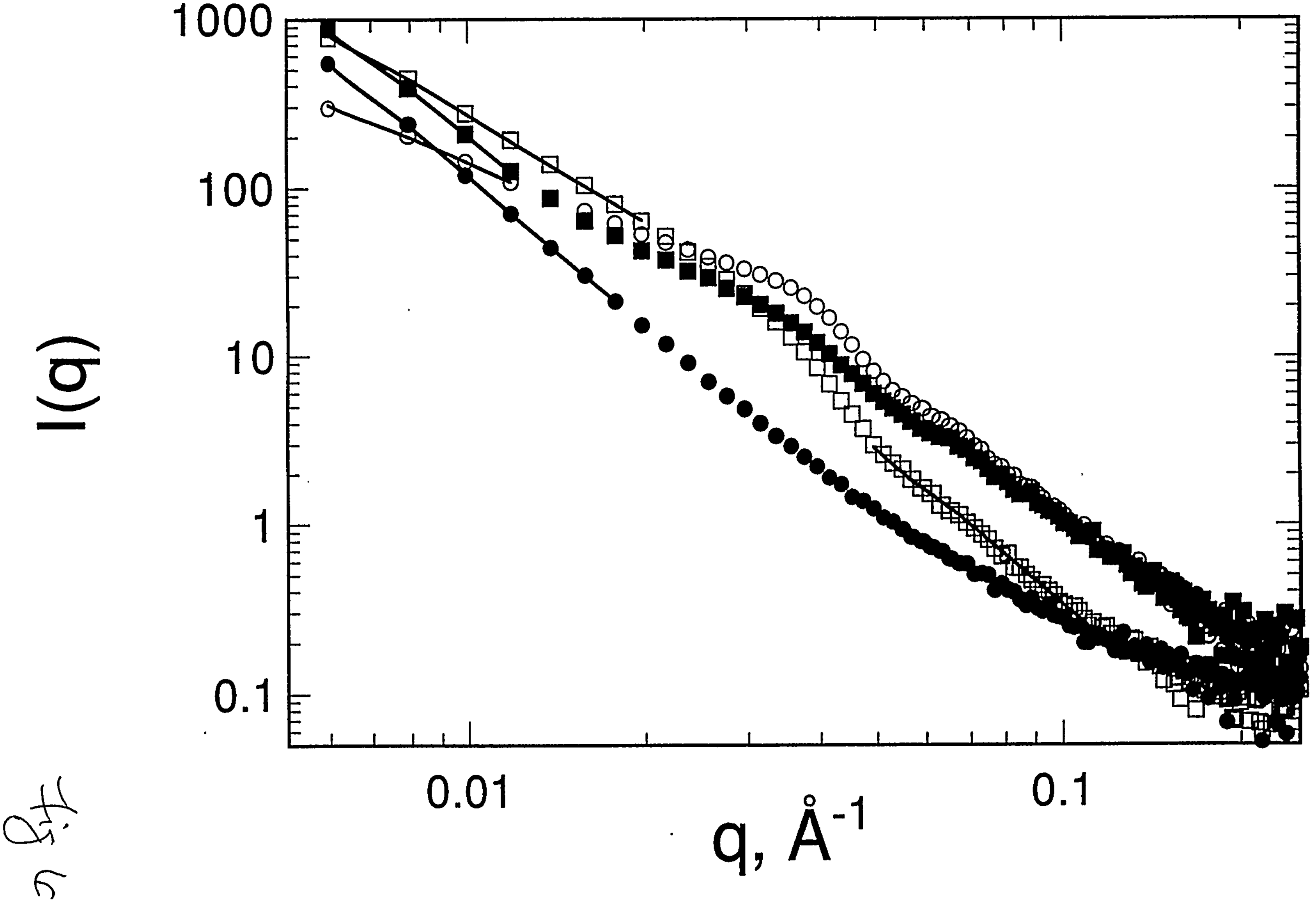

Fig 6