Interfacial Phenomena in Macromolecular Systems. I. Heats of Adsorption of Polysiloxanes on Modified Silica Surfaces

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ABSTRACT: Heats of adsorption at approximately zero surface coverage of low molecular weight linear and cyclic methylsiloxanes have been measured on a silica surface using vapor phase chromatography. The silica surface was modified by reaction with several alcohols and chlorosilanes. These surfaces were characterized in terms of heats of adsorption of a model compound, octamethylcyclotetrasiloxane. Modified surfaces gave heats of adsorption which were lower by several kilocalories as compared to the unmodified silica and which changed according to the nature of the alkyl group and the extent of surface coverage. These results were compared with those obtained on polyethylene powder and revealed the existence of long range (more than one molecular diameter) interaction energy between siloxane compounds and the silica surface.

It is generally recognized that the chemical nature of a filler surface is important in determining the physical properties of filled composites.[1,2] However, complete agreement on the exact nature of the polymer–filler interfacial bonding is lacking and as a result no quantitative theory relating the interfacial energy to the physical properties of the composites exists.

The nature of the interfacial bonding is but one factor determining the physical properties of the composites; the others are particle size and "structure"[3-6] and dispersion of the filler in the rubber matrix. The interdependence of the variables has been discussed by Kraus in a recent review.[2] However, it is difficult to separate the effects of these variables, since the exact role of each is hard to evaluate.

The work reported here was undertaken in order to establish more clearly the nature of the interaction between silica and polydimethylsiloxanes. The objective was to change their interaction energy without changing the particle size. Furthermore, we hoped to obtain several samples with different surfaces but with similar interaction energies. This study describes methods of changing the interfacial energies of silica fillers and the nature of the changes accomplished It also describes the reactions with the functional groups on the filler surface and the correlation of the changes in the interfacial energy with the extent and nature of the coverage. In a future paper we will relate the effect of these changes to the physical properties of the composite.

Method

The system consisted of low molecular weight polydimethylsiloxane compounds which were used as the polymer model, and silica as the filler.

The Model Compounds. To facilitate characterization of the interaction energy of a large number of surfaces, the choice of a model compound method became necessary. Octamethylcyclotetrasiloxane (D_4) was chosen as the model compound for the polydimethylsiloxanes because it is (a) homologous with the polymers, (b) free from strain energy, (c) free from end groups, and (d) suitable for the experimental method used. Low molecular weight linear and other cyclic compounds were also used in some of the work described.

Silica. An amorphous, thermal silica, Cab-o-Sil M-5, particle size 12 mμ, manufacturers' quoted surface area 200 m^2/g, was selected as the filler (measured value by B.E.T. 199 ± 10 m^2/g).

Theory

The heat of adsorption of the model compound on the silica surface was taken as a measure of the interaction energy between a silica filler and a polydimethylsiloxane. The so-called pulse elution technique of vapor phase chromatography was used to determine isosteric heats of adsorption at approximately zero surface coverage. Beebe[7] and Ross[8] have developed the necessary theory of this method. Here, only the essential equations of the theory will be given while the experimental details will be discussed fully.

The theory is based on application to an ideal system, where it is assumed that the adsorption isotherm is linear. The slope (α) of the linear portion of the adsorption isotherm (a plot of the volume of materials adsorbed per gram of adsorbent *vs.* pressure) is related to the retention time of the adsorbed species at a given column temperature (T_c) as

$$\alpha = (t_r - t_d)F273/(T_fW)$$

where t_r = retention time of the adsorbed species (minutes), t_d = retention time of the reference or nonadsorbed species, air (minutes), F = flow rate of the carrier gas, He (cubic centimeters per minute), T_f = temperature of the flow meter (degrees Kelvin), W = total weight of the adsorbent present in the column (grams).

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Since $\alpha = v/p$, where v is the volume of the gas adsorbed in cubic centimeters (STP) per gram of adsorbent and p is the corresponding equilibrium pressure, the Clausius Clapeyron equation may be written as

$$\left(\frac{\mathrm{d} \ln v/\alpha}{\mathrm{d}T_c}\right)_v = \frac{\Delta H}{RT_c^2}$$

where ΔH is the isosteric heat of adsorption. Integration of this equation gives $\ln v/\alpha = -(\Delta H/RT_c) + A$, which at constant volume reduces to $\ln \alpha = (\Delta H/RT_c) + B$, where A and B are constants. Thus by plotting $\ln \alpha$ against $1/T_c$, the isosteric heat of adsorption, ΔH, may be obtained. Throughout the present investigation F was held constant at 60 cc/min. Since variation in T_f due to changes in the room temperature is small, it was only necessary to plot $\ln (t_r - t_a)$ against $1/T_c$ to obtain ΔH.

Experimental Section

The instrument used was a Beckman GC-2A gas chromatograph equipped with a thermal conductivity detector. Stainless steel tubing, 11 in. in length and 0.25 in. o.d. (about 0.2 in. i.d.) was used as the column. The modified silica (described in the following section), of size fractions remaining between 40 and 80 mesh sieves, was used to pack the columns. The packing procedure was standardized so that the amount of sample required to pack the same length of column was constant within 2%.

Helium gas supplied by Air Reduction Co. was used as the carrier gas, and it was dried by passing it through narrow copper coils cooled with liquid air.

The packed columns were conditioned at about 230° for 3–4 hr at a flow rate slightly in excess of that used during the experiment. Reproducible volumes of the adsorbate ranging from 0.3 μl down to virtually zero were injected into the carrier gas stream with a microliter syringe. Air was used as the reference gas. Since at any given temperature and attenuation of the detector response the peak heights were proportional to the sample size, the latter could be monitored by peak height. Retention time of the adsorbed species relative to that of the air peak could be measured with an accuracy of 0.05 min.

Invariably the retention time varied with the sample size; larger retention times being found for smaller samples. The apparent dependence of the retention time on the sample size is characteristic of many solid–vapor systems. It implies a heterogeneous surface and consequently a nonlinear adsorption isotherm. In the present case it meant that the isotherm was concave toward the pressure axis. For the ideal case, as mentioned earlier, the slope of the isotherm should be constant and therefore the retention time should be independent of the sample size under specified flow and column temperature conditions.

The observed dependence of retention time on the sample size, however, was not serious. The extrapolated value of the retention time at zero sample size could be determined within ±0.1 min. This resulted in an uncertainty of about ±0.2 kcal/mol in the experimental value of ΔH. Because of the convenience and feasibility of the pulse elution technique for determining heats of adsorption of high-boiling temperature liquids, the method was considered an excellent one for the characterization of the surfaces.

Treatment of Silica. 1. Column Packing. In order to be used as a substrate in the chromatographic column, the original powdery silica had to be converted into relatively granular form by wetting it with water and then drying it at 125° under vacuum. This was necessary since very fine powder results in nonsteady flow conditions. After drying, the powder was ground and sieved, and the fraction between 40 and 80 mesh sizes retained to pack the columns. The surface area of the modified silica was determined by nitrogen adsorption and found to be 199 ± 10 m²/g. This indicated no change in the surface area, from the manufacturers' quoted value of 200 ± 25 m²/g, as a consequence of the hydrothermal treatment.

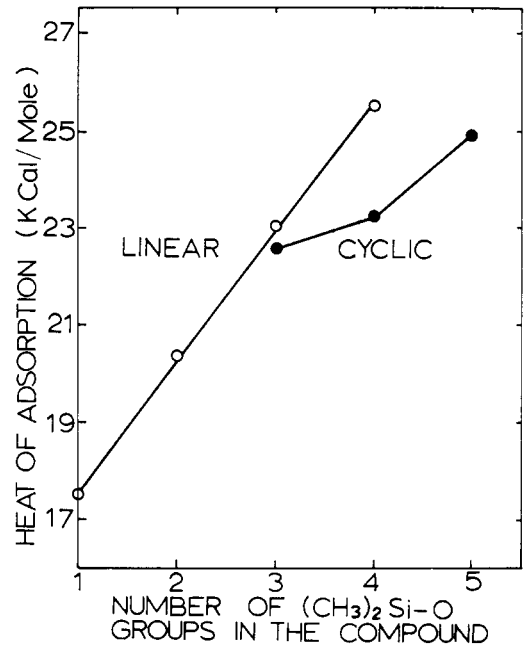

Figure 1. Heats of adsorption of methylsiloxanes on silica.

2. Surface modifications of the silica were accomplished by heating in the presence of alcohols and other species which were expected to react chemically and be retained on the surface. Because of the high pressures generated at elevated temperatures, most treatments of the modified silica with various alcohols had to be carried out in the liquid phase in a bomb. The extent of the treatment and the resultant surface coverages depended on the temperature of the treatment which was varied from 100 to 300°. The treatments with alkyl chlorosilane were done in solution in hexane. The surface coverage in that case depended on the concentration of the solution.

After the surface treatments, the silica samples were recovered and dried. In the case of high molecular weight alcohols, the samples were washed with hexane before drying. Drying was done at 230° in a stream of dry helium for 2–3 hr. Samples were taken for analysis for total carbon. The surface coverage (θ) in terms of the number of alkoxy groups per 100 Å² was calculated according to the formula

$$\theta = \frac{6.02 \times 10^{23} \times c}{n \times 12 \times 199.7 \times 10^{18}}$$

where c = grams of carbon per gram of silica and n = number of carbon atoms in the alkoxy groups. Results of total analysis were reproducible within 10%.

Self-supporting disks of the treated silica (about 30 mg) were made and their infrared spectra were taken. The presence of the absorption bands at 2850 and 2960 cm^{-1} indicated the presence of the alkoxy groups on the silica surface. The intensity of the bands increased with the temperature of the treatment and thus qualitatively agreed with the results obtained by the total analysis.

Results and Discussion

The Adsorption of Methylsiloxanes on Untreated Silica. In Figure 1 are plotted heats of adsorption at

approximately zero surface coverage of linear and cyclic methylsiloxanes. It is obvious from these high heats of adsorption that the interaction between silicones and silica surface is very strong. Another point of interest, readily discernible from this plot, is that the linear compounds appear to have higher heats of adsorption than the cyclic compounds. However, the observed difference may not be quite as marked as it first appears, from Figure 1, if we consider that omitted in the case of the linear compounds are $CH_3Si(CH_3)_2$ and $-CH_3$ groups or the equivalent of tetramethylsilane. Hexamethyldisiloxane (MM) has a heat of adsorption of 17.6 kcal/mol, roughly 9.2 kcal/mol in excess of its heat of condensation.[9] What the exact contribution of $CH_2Si(CH_3)_2$ and $-CH_3$ groups relative to Me_2SiO is in this case it not known, but it could be sufficient to account for the observed difference of 2.3 kcal/mol in the heats of $Me_3Si(OSiMe_2)_3OSiMe_3$ and $(Me_2SiO)_4$, both of which have four Si–O linkages. With the exception of the cyclic trimer (D_3), the heats of adsorption of both the linear and the cyclic compounds increase linearly with the number of Me_2SiO groups. An extrapolation from the values observed for D_4 and D_5 shows that the value for D_3 is unduly high. This could well be due to the ability of the coplanar D_3 to conform more completely to the surface of the silica.

The increase in heat of adsorption per (Me_2SiO) unit is of the order of 2.7 kcal/mol in the case of the linear compounds. The difference in the heats of adsorption of D_5 and D_4 is only 1.7 kcal/mol. The difference between these values is significant from the point of view of the experimental error ($\simeq$0.2 kcal/mol) and what it represents is not quite clear at present. It may reflect greater flexibility of a linear molecule as compared to a cyclic compound.

Since the entire amounts of the samples injected into the column during these experiments were recovered and no spurious peaks were observed, it is believed that the interaction between the silicones and the silica surface is primarily physical. It may, however, be added that when a fresh column was prepared it was noticed that small fractions of the first couple of samples were retained on the silica and were presumed chemisorbed.[10] The surface coverage calculated on the basis of the total amount of the sample retained in this manner by the silica amounted to less than 10^{-3} of a monolayer and consequently was not detected by infrared spectroscopy. It is therefore not considered important in the present discussions.

The energetics of the adsorption should be considered in the light of the surface characteristics of the filler and the chemical nature of the silicone compounds. A fully hydrated silica surface carries as many as six to eight hydroxyl groups per square mμ.[11,12] Because of the participation of the d valency in the electronic shell of the silicon atom and the resulting delocalization of charge in the silica matrix, the silanol groups on the silica surface are strongly protonized.[13] Therefore, the molecules with electron donating or proton accepting power can interact strongly *via* charge transfer or π coupling while saturated compounds, which are incapable of charge transfer, are limited to interaction due to the dispersion forces only.

The perturbation of the stretching frequency of the surface hydroxyl groups (3750 cm^{-1}) has been used as a measure of the interaction energy of molecules adsorbed on the silica surface. Basila and MacDonald[13,14] showed little perturbation to be caused by argon and cyclohexane adsorption, while benzene and mesitylene caused major shifts in the absorption frequency. Kiselev[15,16] related these shifts to the ionization potentials of the adsorbing species and formulated a quantitative relationship between the size of the frequency shift and the heat of adsorption (the net ΔH_{ads} being defined as the difference between the heat of adsorption of a compound on a fully hydroxylated and a dehydroxylated surface). The net heat of adsorption is therefore a measure of the specific interaction between the adsorbed molecules and the hydroxyl groups. The heats of adsorption of the compounds used in this study (Figure 1) can now be considered in the light of the above.

Since siloxane compounds possess π-bonding character involving the ultimate dπ and pπ orbitals of the silicon and oxygen atoms, respectively,[17] it would be expected that they would be capable of the strong interaction which we observed with the completely hydroxylated silica surfaces.

Adsorption of Octamethylcyclotetrasiloxane (D_4) on Surface Modified Silicas. Having established the quantitative interaction energy of siloxanes on a pure silica surface, investigations were then initiated into the influence of surface coverage on this interaction energy. Octamethylcyclotetrasiloxane, D_4, was adsorbed on samples whose surfaces had been modified in various ways and to various extents, and the effects of these modifications on the adsorption energy were measured.

Changes in the surface of silica invariably require reaction of the surface hydroxyl groups. These groups, in addition to being strongly protonized, are present in various geometrical and physical states and thus render the surface energetically nonuniform.[18] They may be either hydrogen bonded to one another or free from such bonding. Those bonded to one another can be partially removed by dehydration as a result of condensation of the adjacent hydroxyl groups and the elimiation of water.[14,15] The free hydroxyl groups are, however, more reactive than the bonded groups, and these can be reacted with alcohols and with chlorosilanes.[11,16,19,20]

The reactions of alcohols and mono- and dichloro-

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silanes have been described by Iler, *et al.*,[20] by Lowen[11] and by Kiselev.[16,19,21-23] In all cases where the surface energetics of the modified silicas were studied,[11,21-23] there was observed a reduced interaction energy, as indicated by diminished retention volumes of several polar and strongly interacting compounds. For example, the net heat of adsorption of benzene on a silica covered with a single complete layer of trimethylsilyl groups was reduced to zero from a value of 5 kcal/mol on the unmodified silica.

The heats of adsorption of D_4 on silica treated with various normal alcohols are plotted in Figure 2. Though the surface covered with the alkyl groups gave lower interaction energy as compared to the untreated surface, the lowest values obtained with different treatments are still appreciably higher than the heat of condensation of D_4. The heat of condensation of D_4 is 10.9 kcal/mol at 125°.[24] This is the temperature range at which heats of adsorption measurements were done for treatments giving maximum coverages of the alkyl groups. It is obvious that a fewer number of larger groups are as effective in reducing the heat of adsorption, to a given value, as a large number of smaller alkoxy groups.

Similar conclusions may be reached from the results of Figure 3 where the heats of adsorption of D_4 on silica treated with chlorosilanes are plotted. At a given coverage, the order of increase in effectiveness in lowering the heats of adsorption is as follows: $CH_3HSiCl_2 < (CH_3)_2SiCl_2 < (CH_3)_3SiCl$.

Even though none of the treatments involving normal alcohols reduced the heat of adsorption (ΔH) of D_4 down to its heat of condensation (ΔH_v), it appears that if the individual curves (Figure 2) were extrapolated to maximum possible coverages of the alkyl groups, *e.g.*, 3.8 and 5.6 for butoxy and methoxy groups, respectively,[20] they would reach the value of the heat of condensation. The same could not, however, be said about the treatments involving chlorosilanes (Figure 3). Even at the maximum possible coverage of 2.2 trimethylsilyl groups per square millimicron,[11] the heat of adsorption of D_4 is several kilocalories above its heat of condensation. This is contrary fo Kiselev's work where in a similar experiment he obtained a heat of adsorption of benzene equal to its heat of condensation.[23] It therefore seems that, though the steric effect may be important, the effect of the remaining (hidden) hydroxyl groups can be observed at considerable distances from the surface. More will be said about this in the following sections.

The effect of the nature of the functional groups present on the silica surface on the heat of adsorption of D_4 may be seen in Figure 4. Here the results obtained on silica treated with ethanol and 2,2,2-trifluoroethanol are compared. The electron-rich fluoro groups gave lower heats of adsorption, though the net effect was not very marked. It is difficult to rationalize these results as the effects of these groups on the specific and non-

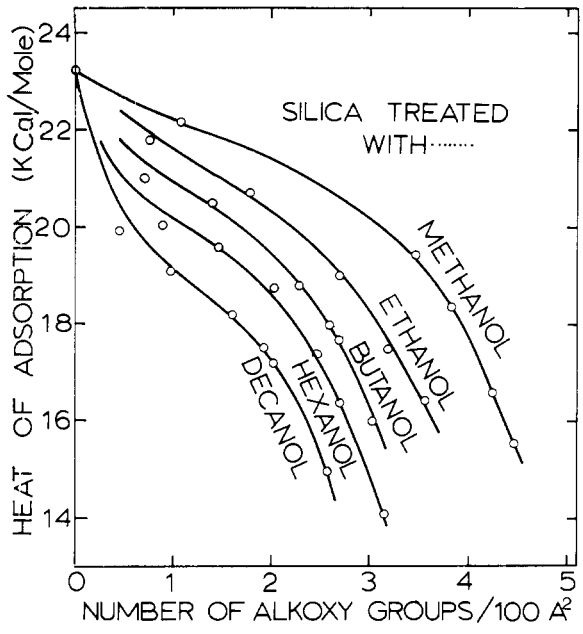

Figure 2. Heats of adsorption of octamethylcyclotetrasiloxane on silica surfaces modified with linear alcohols.

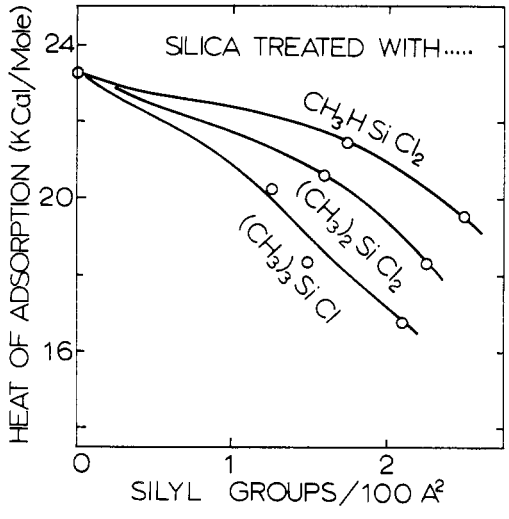

Figure 3. Heats of adsorption of D_4 on silica surfaces modified with alkyl chlorosilanes.

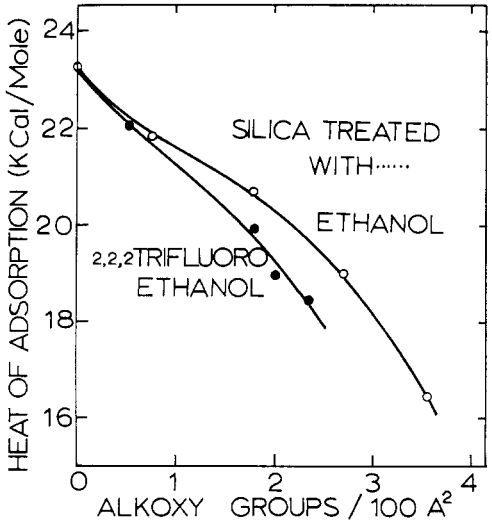

Figure 4. Heats of adsorption of D_4 on silica surfaces modified with fluoroethanol.

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TABLE I
HEATS OF ADSORPTION OF D_4 AND DECANE ON TREATED SILICA AND ON POLYETHYLENE POWDER

Treatment	Surface coverage, groups/100 Å²	Heats of adsorption, kcal/mol: D_4 ΔH	D_4 $(\Delta H - \Delta H_v)^a$	Decane ΔH	Decane $(\Delta H - \Delta H_v)$
None	...	23.3	11.7	15.9	3.7
Ethanol	3.59	16.4	4.8	14.7	2.5
Butanol	3.04	16.0	4.4	14.1	1.9
Hexanol	3.16	14.0	2.4	13.2	1.0
Polyethylene	...	11.6	0.0	12.2	0.0

[a] ΔH_v = heat of vaporization of D_4 and decane.

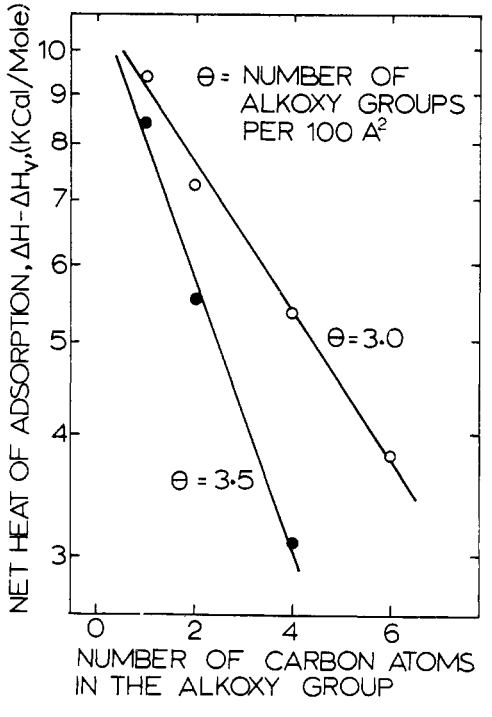

Figure 5. Net heats of adsorption of D_4 on silica *vs.* surface treatment.

specific interactions of D_4 are not known. If one assumes that at equivalent coverages the surface structure (morphological) in both cases would be identical, the fluoro surface would give greater nonspecific (dispersion) interaction because of the heavier fluorine atoms. This would suggest that the alkyl groups have considerable effect (apart from the steric effect) on the specific interactions between D_4 and the silica surface.

In Figure 5 is plotted the net heat of adsorption $(\Delta H - \Delta H_v)$ of D_4 as a function of the number of carbon atoms in the alkoxy groups at fixed coverages. Since each group on the average covers the same amount of the surface area, sweeping a volume element extending into the atmosphere, the effective depths or thickness of the shielding that the D_4 adsorbate molecules would encounter on the surface would be proportional to the number of carbon atoms in the chemisorbed alkyl groups. Exponential decrease in the net heat of adsorption as a function of the size of the alkoxy groups further demonstrates the importance of the steric effects, as one would not postulate an exponential increase in the inductive effect with the size of the alkyl groups.

It may be noted once again that the net heat of adsorption of D_4 on the silica surface is strongly dependent on the number and size of the alkoxy groups present on the surface. For example, the extrapolation of the plots in Figure 5 indicates that, while groups with 14 carbon atoms would reduce ΔH to within 1 kcal of the ΔH_v value, at a coverage of three groups per square millimicron, groups with only eight carbon atoms would be required at a coverage of 3.5 groups per square millimicron.

Theses results are in agreement with those reported by Harkins and Jura. These authors reported an exponential decrease in the energy of desorption of water on nonporous titanium dioxide.[25] They also reported films of thickness of 15, 36, and 64 Å for water, nitrogen, and butane on the same surface at pressures just below saturation. It is therefore entirely possible that the effects of the surface force field could extend over appreciable distances.

To verify further that the above-mentioned residual net heat of adsorption (Figures 2 and 3) was not the results of some experimental artifact, heats of adsorption of decane were determined on silica surfaces with maximum coverages of ethoxy, butoxy, and hexyloxy groups, as well as on polyethylene powder. The results given in Table I show that the heats of adsorption of D_4 and decane follow the same order throughout, except for the case of polyethylene. The value of 12.2 kcal/mol for decane on a polyethylene surface agrees exactly with its heat of condensation. The value of 11.6 kcal/mol for D_4 on polyethylene was determined in the temperature range of 90–110°. Its heat of condensation at 100° is also 11.6 kcal/mol. It therefore proves that the observed long-range interaction indicated by the residual interaction energy of D_4 on treated silica is real.

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