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Surface and Catalytic Characteristics of Thermally and Chemically Activated Bentonite Catalysts Used in the Polymerization of Styrene

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The most active bentonite samples in the polymerization of styrene were found to be one thermally treated for 2 hr at 550°C and one chemically treated with 35% (w/w) H_2SO_4. Surface studies of various bentonite samples showed that the characteristic pore system and Lewis acid sites resulting from the removal of the adsorbed water were responsible for the catalytic activity of the thermally treated bentonite. Overheating could destroy both the catalyst activity and the exposed surface. Upon activating bentonite with H_2SO_4, it was found that both the produced pore system and the creation of new Brønsted acid sites could be responsible for the catalytic activity. The different factors affecting the polymerization reaction over the most active samples and the dependence of the structure of the produced polymer on the pretreatment of the bentonite were also investigated.

1. INTRODUCTION

Synthetic and natural clays of the montmorillonite group are now widely used in chemical industry as catalyst supports (*1*), as well as catalysts for many reactions, e.g., alkylation (*2*), isomerization (*3*), and polymerization (*4*).

In the majority of the catalytic reactions studied, it was found that the activity of the montmorillonite clays, and in particular bentonite, increases markedly after subjecting these clays to certain treatments in which either physical or chemical methods are used (*5*).

The study of the thermal treatment of these clays at relatively low temperatures showed that, in most cases, elimination of the adsorbed water occurs, whereas at higher temperatures a loss of water of constitution takes place (*6*, *7*). It was found out also that a rapid loss of hydroxyls was observed around 500°C and was practically complete at 800°C. Judging from X-ray diffraction data, Warshaw *et al.* (*8*) showed that, on heating the mineral to the dehydroxylation temperature, the whole structure remained almost unchanged. However, it was reported recently (*9*) that the structure of the studied bentonite is affected, to varying degrees, by treatment at sufficiently high temperatures.

On the other hand, the chemical activation of these clays was studied by several investigators who showed that it can be effected by acids, e.g., H_2SO_4 (*10*, *11*) and dilute HCl (*12*), or alkalies, e.g., Na_2CO_3 (*13*). As has been proved by X-ray studies, electron microscopy, and DTA, it was

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found that during acid treatments the montmorillonite crystal structure was destroyed with the retention of the aluminium silicate layer (*11, 12*).

The use of bentonite as a catalyst for the polymerization reaction was reported by Shephard and his collaborators (*4*), who indicated that both the dimer and the trimer are usually formed. The activity of this mineral was found by Voge (*14*) to be dependent on its ability to accelerate reactions of carbonium ions. Solomon and Rosser (*15*) investigated in detail the polymerization of styrene by sodium, calcium, and cobalt montmorillonites, and concluded that the polymerization by sodium montmorillonite shows the characteristics of both radical and ionic mechanisms. They proposed the formation of a radical–carbonium ion as an initiating step, followed by a rapid dimerization, and then a cationic propagation. The authors also showed that when an organo-clay complex was used, the polymerization was found to proceed cationically, and the produced polymer was formed between the clay laminae, generating the carbonium ions.

In the study carried out by Matsmulo and his co-workers (*16*) on the initiation mechanism of the polymerization of styrene, no evidence for the presence of an organic free radical was found by ir or by NMR studies. The authors indicated that the ratio of the rate constant of termination to that of propagation was 1.3×10^{-2} and that the apparent activation energy in the studied temperature range (−20–10°C) was 4.1 kcal/mol. They also suggested that the polymerization process proceeded, under the studied conditions, via a cationic mechanism, whereas initiation took place by Brønsted acid sites. In a series of investigations carried out by Bittles *et al.* (*17–19*), the rate of polymerization of styrene over an acid clay was studied, and a product having a molecular mass of 500 to 2000 was found to be formed.

From the foregoing discussion, it may be expected that the conditions of the activation by the use of previously mentioned methods have a great influence on both the surface and the textural characteristics of the studied bentonite catalyst. This influence, in turn, seems to be reflected directly on the catalyst activity, thus affecting the nature and the structure of the produced polymer. Although some work has been reported in this direction, the information available seems to be incomplete.

The present investigation deals mainly with the study of the different conditions of activation with the aim of finding out the most active catalyst samples in the process of the polymerization of styrene. The surface characteristics of the various bentonite samples were investigated by means of low-temperature adsorption of nitrogen and X-ray diffraction analysis. The different factors affecting the polymerization reaction were then studied over the most active catalyst samples. The dependence of the product structure on the pretreatment of the catalyst and its textural characteristics was one of the important parameters taken into consideration in the present work.

2. EXPERIMENTAL

2.1. MATERIALS

(a) Styrene Monomer

Styrene used in the present investigation was a Prolabo product stabilized by 0.001% (v/v) *p*-tertio isobutyl pyrocatechol. The stabilizer was removed by shaking with 10% caustic soda, followed by washing several times with distilled water till free from alkali. Styrene was dried by standing over anhydrous sodium sulfate for 48 hr, then filtered and distilled at 48°C under a nitrogen atmosphere at a reduced pressure. The first and the last third fractions were discarded. The product was stored at −20°C.

(*b*) *Bentonite Clay*

Bentonite clay used as a catalyst in the present investigation was also a Prolabo laboratory chemical and was subjected to the following treatments.

(*i*) *Thermal activation.* In this process, the clay sample was heated at 550°C for different times, namely, 1, 2, 3, and 4 hr in a tubular furnace in presence of a stream of dry air flowing at a constant rate (*20*). The samples were designated as B_t-0, B_t-1, B_t-2, B_t-3, and B_t-4, corresponding to the fresh untreated bentonite and its samples activated for 1, 2, 3, and 4 hr, respectively.

(*ii*) *Chemical activation.* In this process, according to Milliken's method (*20*), the clay was treated thermally for 2 hr at 550°C, then activated chemically with H_2SO_4, the initial concentration of which was 20% (w/w), and finally it was again treated thermally at 550°C. The technique adopted for the acid treatment involves continuous stirring of the thermally treated bentonite sample with varying amounts of the acid for 6 hr at 90–95°C. The amounts of the acid used were 25, 35, and 45% by weight of that of the clay. The catalyst samples activated by this method were designated as B_c-25, B_c-35, and B_c-45, thus corresponding to the percentage of acid used.

2.2. Polymerization of Styrene

The polymerization of styrene was carried out either in solution or in bulk.

(*a*) *Polymerization in Solution*

Styrene in benzene solvent was refluxed for 5 min in an oil bath adjusted to the required temperature, then an accurately weighed amount of the activated catalyst was added while stirring. The concentration of the catalyst ranged from 0.1 to 2% (w/w). The reaction was allowed to proceed for the required time at a constant temperature, in the temperature range of 60 to 80°C, after which the solution was filtered to remove the catalyst. The polymer was precipitated by running the solution in a calculated amount of methanol (10 ml of alcohol for each 1 ml of the reaction mixture) with occasional stirring. With the aim of purifying the formed polymer, the product was dissolved in dioxane (30 ml for each 1 g of polymer) and was then reprecipitated in methanol. The purified polymer was filtered and dried under vacuum at 40°C until reaching constant weight.

(*b*) *Polymerization in Bulk*

The freshly distilled styrene was introduced into the polymerization tube with a weighed sample of activated bentonite under a dry flow of nitrogen. The reaction tube was sealed and then placed in a thermostat adjusted to 80°C for the required time, after which it was cooled to room temperature. The tube was carefully opened, and the formed polymer was dissolved in benzene with occasional shaking. The polymer was then precipitated and purified in the same way mentioned above for polymerization in solution.

2.3. Estimation of Catalytic Activity

The catalytic activity was expressed in the present investigation in terms of percentage of the polymer yield, which was calculated according to the following equation:

$$\text{Yield}(\%) = w/s \times 100,$$

where w is the weight of the formed polymer and s is the weight of the styrene monomer.

2.4. Viscosity Measurements and Determination of the Molecular Weight of the Polymer

The specific and intrinsic viscosities of the polymer solutions were determined by applying Huggin's equation (*21*) in the form:

$$\eta_{sp.}/C = [\eta] + K[\eta]^2C,$$

where η_{sp}/C is known as the reduced viscosity which is a function of the molecular weight (η_{sp} is the specific viscosity for the given polymer concentration C expressed in grams per 100 ml of solution), η is the intrinsic viscosity which is considered as a limiting value of the reduced viscosity, and K is the Huggin's constant, which is characteristic for the used solvent.

The specific viscosity, η_{sp}, was measured for different polymer concentrations by using the suspended level Ravikov viscometer (*22*). For the determination of the intrinsic viscosity, η, the values of η_{sp}/C were plotted versus the concentration C, and the obtained straight line was extrapolated to zero concentration. The Huggin's constant, K, was also calculated from the slope of this line.

2.5. Determination of Specific Surface Areas and Pore Structure Analysis

Adsorption–desorption isotherms of pure nitrogen on the surface of different bentonite samples were measured at −196°C using a conventional volumetric apparatus. Specific surface areas were calculated from the isotherms by applying the BET equation (*23*). The pore structure was analyzed on the basis of the adsorption data by the aid of the MP method (*24*) and the corrected modelless method (*25*).

2.6. Infrared Spectral Study of the Formed Polymer

A spectrophotometer, Model Sp-200 G (Unicam), was used for the ir-spectral study of the different samples of the produced polystyrene.

2.7. X-Ray Diffraction Analysis

The different samples of the bentonite catalyst as well as the different samples of the produced polystyrene were examined by using a Philips X-ray diffractometer, Model PW-1010.

3. RESULTS AND DISCUSSION

3.1. Characterization of Various Bentonite Samples Used in Polymerization of Styrene

(*a*) *Catalytic Activity*

The results of the catalytic activity of various bentonite samples, measured in the polymerization of styrene, are summarized in Table 1, where the activity is expressed in terms of polymer yield (%). In the polymerization experiments of series I, the catalyst concentration was 0.5% (w/w) and the monomer concentration was 20% (w/w), whereas in the experiments of series II, the catalyst concentration was 0.2% (w/w) and the monomer concentration was 33.3% (w/w). The effect of the concentration of both the catalyst and the monomer on the polymerization reaction will be discussed later in this investigation. The polymerization reaction was carried out at 80°C using the above mentioned procedure, and the polymer yield in each experiment was determined after 48 hr from the start.

TABLE 1

The Catalytic Activity of Various Activated Bentonite Samples Measured in the Polymerization of Styrene

Series I (Thermal activation)		Series II (Chemical activation)	
Catalyst sample	Polymer yield, (%)	Catalyst sample	Polymer yield, (%)
Without catalyst	8.0		
B_t-0	7.9		
B_t-1	14.0	B_c-25	10.3
B_t-2	20.9	B_c-35	37.0
B_t-3	15.0	B_c-45	35.0
B_t-4	14.7		

It is clear from Table 1 that the most active bentonite samples were the ones which were thermally activated for 2 hr or chemically activated with 35% (w/w) H_2SO_4. From the same table it is clear that the acid-treated samples were much more active than the thermally treated ones. On the other hand, the untreated bentonite was completely inactive.

(*b*) *Surface Characteristics*

(*i*) *Specific surface areas.* From the foregoing investigation, it was observed that the most active catalyst samples were B_t-2 and B_c-35. Consequently, it was found necessary to study the surface characteristics of these two samples and to compare the results of this study with those obtained from studies of the less active samples, namely, B_t-0, B_t-4, B_c-25, and B_c-45.

The adsorption–desorption isotherms of nitrogen are illustrated in Fig. 1 for untreated bentonite and for the different treated samples. Evacuation of all the samples for 3 hr at room temperature at a pressure of 10^{-5} mm Hg was adopted as a standard pretreatment. It is clear from Fig. 1 that all the isotherms are of type II of Brunauer's classification (*26*), forming closed hysteresis loops.

The calculated specific surface area (S_{BET}) are given in Table 2, from which it is clear that the surface areas of the samples B_t-2 and B_c-35 are larger than those of the other samples. On the other hand, the total pore volume, V_p, estimated from the saturation values of the adsorption isotherms, showed a value for sample B_t-2 larger than that of either B_t-0 or B_t-4. As for sample B_c-35, it was found that its V_p value was smaller than those of samples B_c-25 and B_c-45.

(*ii*) *Pore structure analysis.* Reference *t* curves were constructed by several investigators for the adsorption of nitrogen on nonporous solids. For each catalyst sample, an appropriate *t* curve was chosen on the basis of the BET-C constants, which in each case should be of the same order in both the reference *t* curve and the catalyst sample under investigation.

In the present study the *t* curve of Cranston and Inkley (*27*) was adopted

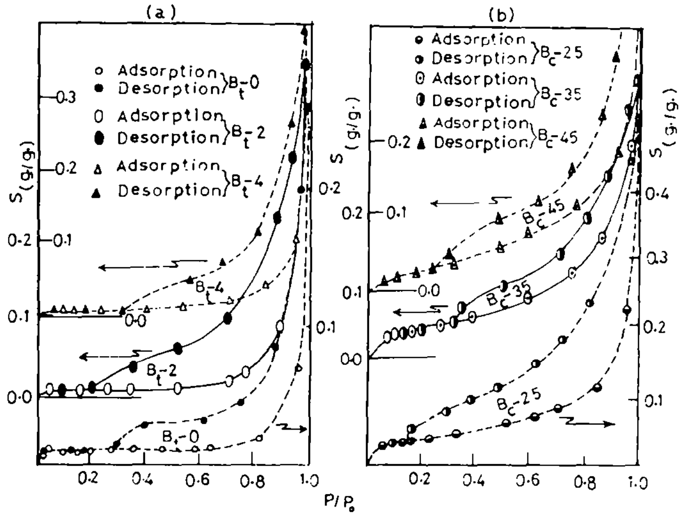

FIG. 1. Nitrogen adsorption-desorption isotherms on the surface of (a) untreated bentonite, B_t-0, and thermally treated samples, B_t-2 and B_t-4, and (b) chemically treated samples, B_c-25, B_c-35, and B_c-45.

TABLE 2

Surface Characteristics BET-C of the Different Samples of Bentonite from the Adsorption Data of Nitrogen

Catalyst sample	BET C constant	S_{BET} (m²/g)	S_t (m²/g)	S_{cum}^{pp} (m²/g)	V_{cum}^{pp} (ml/g)	V_p (ml/g)
B_t-0	90	20.5	20.0	22.7[a]	0.3398[b]	0.3261
B_t-2	12	29.0	31.5	34.7[c]	0.6247[d]	0.5995
B_t-4	13	26.6	25.7	26.0	0.5317	0.5310
B_c-25	27	108.0	112.0	108.0	0.6015	0.6125
B_c-35	48	121.8	120.0	119.4	0.5065	0.5136
B_c-45	14	104.3	104.0	107.7	0.6334	0.6452

[a] $S_n = 12.0$ and $S_w^{pp} = 10.7$ m²/g.

[b] $V_n = 0.0056$ and $V_w^{pp} = 0.3342$ ml/g.

[c] $S_n = 16.5$ and $S_w^{pp} = 18.2$ m²/g.

[d] $V_n = 0.0077$ and $V_w^{pp} = 0.6169$ ml/g.

for the adsorption of nitrogen on the original untreated bentonite, B_t-0. The t curve of Mikhail *et al.* (*24*) was applied for samples B_t-2, B_t-4, B_c-25, and B_c-45, whereas for sample B_c-35, the t curve of de Boer *et al.* (*28*) was used.

From the adsorption data, V_l–t plots were constructed, where, V_l is the volume of nitrogen in milliliters per gram and t is the statistical thickness in Å. A straight line passing through the origin was obtained in each case. The slope of this line gave the specific surface area, S_t, in square meters per gram. The agreement between S_{BET} and S_t was the main criterion for the correct choice of the t curve used in the analysis (Table 2).

For samples B_t-0 and B_t-2, the obtained V_l–t plots showed both the downward and upward deviations, indicating the existence of both micro- and mesopores. In the other samples, only mesopores seemed to exist, since only upward deviation was detected from the V_l–t plots. The micropores were analyzed by the use of the MP method (*24*), while the mesopores were analyzed by the aid of the corrected modelless method (*25*).

The results of pore structure analysis are summarized in Table 2, where the cumulative values of surface area, S_{cum}, and of pore volume, V_{cum}, were calculated for the samples B_t-0 and B_t-2 by adding the values characterized for mesopores, i.e., S_w and V_w to those of micropores, i.e., S_n and V_n. For the other samples, the cumulative values were those of the mesopores only, assuming a parallel plate model, for which the suffix (pp) was used.

The pore-size distribution curves for the various catalyst samples are shown in Fig. 2, and they represent the distribution

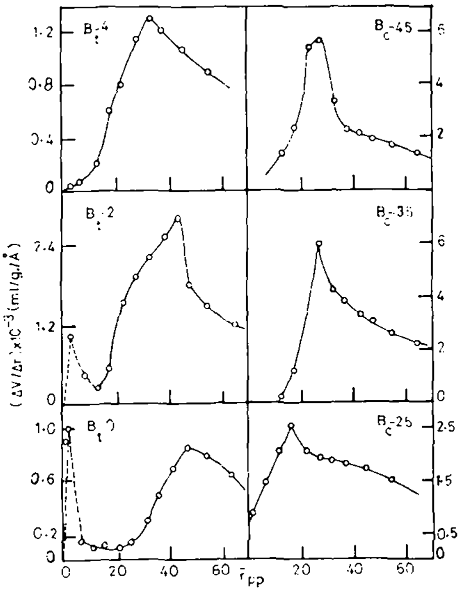

FIG. 2. Pore-size distribution curves for untreated bentonite and the various activated samples.

of pore volume ($\Delta V/\Delta r$ in milliliters per angstrom) as a function of the mean hydraulic radius ($\bar{r}_{h(pp)}$ in angstroms). These curves reflect the following features: (i) In the original untreated bentonite, B_t-0, a group of micropores existed together with a group of mesopores, having a most frequent hydraulic radius of 48 Å. (ii) In sample B_t-2 which was treated thermally for 2 hr at 550°C, a slight narrowing of pore radius took place, viz., from 48 to 42 Å. Although the fraction of the micropores was the same as in the untreated sample, the fraction of the mesopores showed a marked increase. (iii) In sample B_t-4 which was treated thermally for 4 hr at 550°C, an additional narrowing of the pore radii of mesopores was observed, viz., from 42 to 32 Å. This was accompanied by a disappearance of the micropores. (iv) As for the chemically treated samples, those which were treated thermally for 2 hr at 550°C before the acid treatment, a marked decrease in the pore radius was obtained, viz., from 42 to 23 Å with a complete elimination of the micropores. It is to be noted that in sample B_c-25, the fraction of mesopores was the same as in sample B_t-2, whereas in sample B_c-35, this fraction increased markedly and in sample B_c-45, it showed a slight decrease.

In general, the results of pore analysis seem to be in harmony with those of catalytic activity, indicating a direct dependence of the catalyst activity on its surface characteristics, and in particular on the pore system produced in each treatment.

(c) *X-Ray Diffraction Analysis of Samples B_t-0, B_t-2, and B_c-35*

The obtained spacings of hk reflections of the original untreated clay, B_t-0, were those characteristic of the sodium form of bentonite. The data from this analysis were in good agreement with those of MacEwan (*29*) for the bentonite with low substitutions of iron and magnesium for aluminium, assuming a typical formula of:

$$[\mathrm{Si}_{7.76}\mathrm{Al}_{0.24}]^{\mathrm{IV}} \times [\mathrm{Al}_{3.10}\mathrm{Fe}_{0.38}{}^{3+}\mathrm{Fe}_{0.04}{}^{2+}\mathrm{Mg}_{0.52}]^{\mathrm{VI}} \times \mathrm{O}_{20}(\mathrm{OH})_4\mathrm{Na}_{0.68}.$$

For the bentonite sample treated thermally for 2 hr at 550°C, B_t-2, the results indicated the anhydrous modification of bentonite. In general, the diffraction data for this sample showed very little change, indicating that the whole structure was almost unchanged, as had been reported previously by Warshaw *et al.* (*8*).

On the other hand, for the chemically treated sample, B_c-35, the diffraction data showed a slight change in the chemical nature, namely, a slight decrease in the content of alumina with the appearance of very small amounts of sulfates. This slight modification in chemical nature due to acid treatment seemed to be responsible for this change in activity.

It may be concluded that, besides the pore system characteristic for each sample studied, Lewis acid sites resulting from the removal of adsorbed water upon heating the bentonite clay could be responsible for the catalytic activity. This activity was destroyed by overheating, as was mentioned by Bittles *et al.* (*18*), during the rearrangement of tetrahedral aluminium to an octahedral configuration with six coordination. On the other hand, upon activating the clay with acids, it seems that both the characteristic pore system and the creation of Brønsted acid sites were responsible for the catalytic activity in the polymerization reaction.

3.2. POLYMERIZATION OF STYRENE OVER THE ACTIVATED BENTONITE SAMPLES, B_t-2 AND B_c-35

(a) *Rate of Polymerization*

The kinetic curves of the polymerization of styrene at different temperatures, namely, 60, 70, and 80°C, over the catalyst

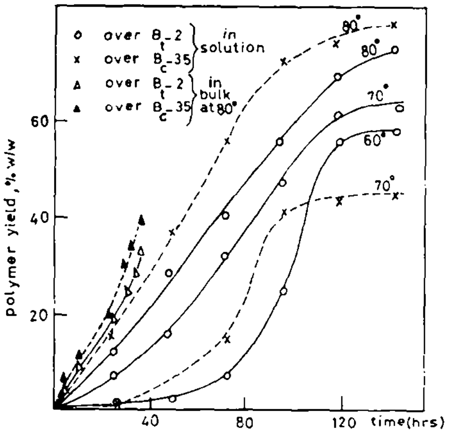

FIG. 3. Kinetic curves for the polymerization of styrene over the activated bentonite samples, B_t-2 and B_c-35, in solution (in the temperature range of 60-80°C) and in bulk (at 80°C).

samples B_t-2 and B_c-35 are shown in Fig. 3. The polymerization reaction was carried out in solution as well as in bulk. The obtained induction periods at 60°C for the sample B_t-2 and at 70°C for the sample B_c-35 could be attributed to the slower initiation steps at these temperatures.[2] The specific viscosity values of the produced polymer solutions indicated that some degradation of the formed long-chain macromolecules took place when the reaction proceeded for long periods, up to 144 hr. The calculated maximum molecular weights of the formed polymers were found to be 135,300 and 228,300 when samples B_t-2 and B_c-35, respectively, were used. An average molecular weight as high as 1×10^6 was obtained when the reaction was carried out in bulk using the catalyst sample B_t-2. In general, the molecular weights of the polymers formed in the present investigation were much higher than those obtained by Bittles *et al.* (*18*) by using Filtrol clay (MW, ~2000).

TABLE 3

The Effect of the Monomer Concentration on Both the Polymer Yield and the Specific Viscosity, η_{sp}

Monomer concentration (%[w/w])	Polymerization over B_t-2		Polymerization over B_c-35	
	Polymer yield (%)	η_{sp}	Polymer yield (%)	η_{sp}
11.1	10.6	0.35	3.8	0.11
14.2	15.1	0.35	9.4	0.33
20.0	20.9	0.39	19.4	0.43
33.3	26.7	0.47	37.0	0.48
100.0	30.0	1.40	38.0	0.62

(*b*) *Effect of Both Monomer and Catalyst Concentrations on Catalytic Activity*

The effect of the different concentrations of styrene monomer on catalytic activity of the samples B_t-2 and B_c-35 is shown in Table 3. The concentration of the catalyst sample B_t-2 was 0.5% (w/w) and that of sample B_c-35 was 0.2% (w/w). The activity was expressed in terms of percentage polymer yield, produced at 80°C. It is clear that the polymer yield and the specific viscosity, η_{sp}, increased gradually by increasing the monomer concentration, reaching their maximum values in bulk polymerization [i.e., 100% (w/w) styrene].

On the other hand, Table 4 summarizes

TABLE 4

The Effect of the Catalyst Concentration on Both the Polymer Yield and the Specific Viscosity, η_{sp}

Catalyst concentration (%[w/w])	Polymerization over B_t-2		Polymerization over B_c-35	
	Polymer yield (%)	η_{sp}	Polymer yield (%)	η_{sp}
0.1	13.6	0.57	24.3	0.49
0.2	27.5	0.54	36.9	0.48
0.5	26.7	0.47	19.5	0.35
1.0	26.1	0.40	12.1	0.03
1.5	23.4	0.36	10.0	0.02
2.0	20.3	0.32	—	—

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[2] A rough treatment of the kinetic curves showed that the rate was practically of zero order at 60° and 70°C and of slightly higher order at 80°C. From the Arrhenius plot, an apparent activation energy of ~13 kcal/mol was obtained.

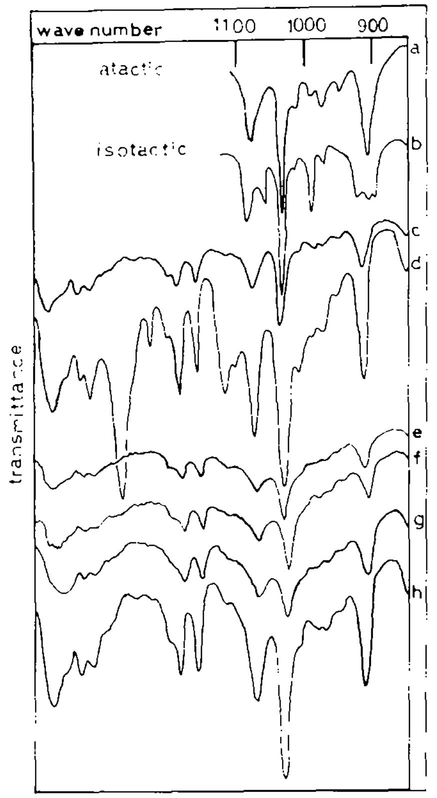

FIG. 4. Infrared spectra of (a) atactic structure, (b) isotactic structure, (c) commercial polystyrene, (d) polystyrene prepared in the presence of benzoyl peroxide initiator, (e) polystyrene formed in solution over B_t-2, (f) polystyrene formed in solution over B_c-35, (g) polystyrene formed in bulk polymerization over B_t-2, and (h) polystyrene formed in bulk polymerization over B_c-35.

the effect of the different concentrations of the activated catalyst on the polymer yield. The catalyst concentration ranged from 0.1 to 2% (w/w), and the initial concentration of the styrene monomer was 33.3% (w/w). The results indicated that the optimum concentration for both samples B_t-2 and B_c-35 was 0.2% (w/w). With a further increase in the catalyst concentration, the polymer yield showed a continuous decrease. However, the specific viscosity, η_{sp}, of the produced polymer solution decreased continuously over the whole range of the catalyst concentration used. It may be suggested, therefore, that the increase in the catalyst concentration resulted in an increase in the density of the active sites. This might lead to a higher degree of conversion of styrene to a low molecular weight species and consequently to a lower yield of high molecular weight polymer.

(c) *Structure of the Formed Polymer and Mechanism of Polymerization*

The tacticity of the formed macromolecules plays the main role in determining the physicochemical and mechanical properties of the formed polymer. It is well known that an ionic mechanism leads to the formation of macromolecules of regular structure, namely, isotactic or syndiotactic configurations. An isotactic configuration is usually formed at low temperatures and in nonpolar solvents, while elevation of temperature and/or increasing the polarity of the medium helps in the formation of syndiotactic configurations. On the other hand, an atactic configuration (or random configuration) is generally obtained in free-radical polymerization reactions.

(*i*) *Infrared spectra of the formed polymers.* Typical ir spectra of atactic and isotactic structures, as well as those of commercial polystyrene, are shown in Fig. 4. The ir spectra of polystyrene formed under different experimental conditions, viz., in solution and in bulk in presence of different catalyst samples, are also shown in this figure.

According to Zbindin (*30*), the spectrum of an isotactic structure is characterized by the presence of an absorption band at 9.45 μm, and the degree of isotacticity can, thus, be calculated from the measurement of the relative amplitude of this band. This band, however, disappears in the spectra of syndiotactic and atactic structures which are almost similar to each other.

From the results obtained, it becomes

clear that the formed polystyrene, in all the cases studied, is characterized by a low degree of isotacticity indicating that it is mostly of atactic or syndiotactic structure.

(*ii*) *X-ray diffraction analysis of the formed polymers.* The results of XRD analysis of the different samples of polystyrene produced under different conditions, viz., in solution or bulk polymerization and by using different catalyst samples, are shown in Fig. 5. It was found from this figure that the structure of the polystyrene produced in the presence of a benzoyl peroxide initiator is different from those of the other polystyrene samples. It may be suggested, therefore, that the mechanism of polymerization in the presence of benzoyl peroxide is different from the one taking place over activated bentonite samples. This may lend further support to the previously mentioned findings of Bittles *et al.* (*18*), that the polymerization of styrene over activated bentonite samples is of ionic mechanism, since it is known that in the presence of benzoyl peroxide the reaction proceeds through a free-radical mechanism.

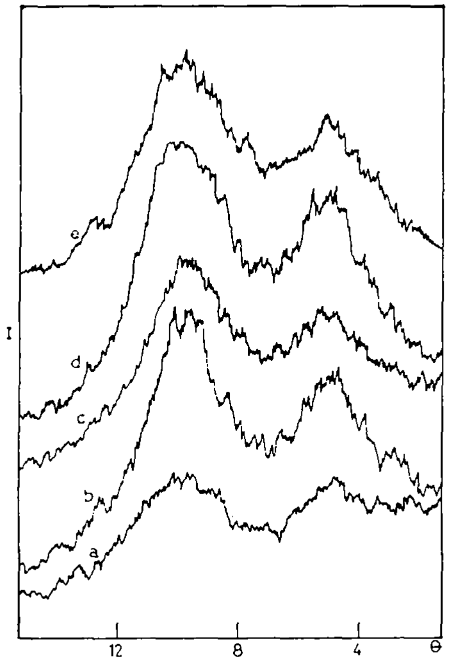

FIG. 5. XRD diagrams of polystyrene prepared by using (a) benzoyl peroxide, (b) catalyst sample B_t-2 in solution, (c) catalyst sample B_t-2 in bulk, (d) catalyst sample B_c-35 in solution, and (e) catalyst sample B_c-35 in bulk.

Analysis of the data obtained on the basis of the previously obtained results of Brawn *et al.* (*31*) shows that the structure of polystyrene, in all the cases studied, is mainly syndiotactic and/or atactic. It is supposed that the obtained polymer has, most likely, a syndiotactic structure and that its formation, as was already mentioned, is favored by the given reaction conditions.

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