Catalytic polymerization of Acrylonitrile by Khulays Bentonite

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Abstract

The aqueous polymerization of acrylonitrile (AN) catalyzed with exchanged Khulays bentonite . The influence of various polymerization parameters (e.g., concentrations of Potassium Persulfate ($K_2S_2O_8$) and monomer , various of organic solvents, and different temperature has been investigated. It was found that the rate of polymerization of AN was found to be dependent on monomer concentration ,initiator and temperature. The activation energy of polymerization was calculated .Thermal properties of the polymer were studied by TGA and DSC techniques. © 2007 CREC UNDIP. All rights reserved.
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1. Introduction

Clays are laminar phyllosilicates that represent a low-cost, accessible alternative for catalytic supports, which are susceptible of being modified for obtaining improved properties. The reactions catalyzed by clays are carried out under mild conditions, the work up procedure is simple as the separation of the spent catalyst is achieved by filtration, and the product is recovered by mere evaporation of solvent. Further, the clays catalysts can be regenerated easily and reused. In particular, the microporous structure and surface acidity of those materials is of great interest for carrying out reactions such as catalytic cracking [1-2], esterification [3], alkylation [4-5], nitration [6], dehydration [7-8], and polymerization catalysis [9-11]. These catalysis have found use in industrial processes such as alkylation of phenols and dimerization and polymerization of unsaturated hydrocarbons[12].

The present papers examines the ability of treated Khulays Bentonite clays to catalyze polymerization of acrylonitrile (AN). The rate polymerization by using different concentrations of $K_2S_2O_8$ initiator and monomer, various of organic solvents, and different temperature were studied.Thermal analyses of the resultant product after polymerization have been performed by Thermogravimetry (TG) and differential scanning calorimetry (DSC). The monomer of acrlyonitrile was selected because its copolymers with others polymers have wide industrial applications in surface coatings technology [13], hemodialysis [14], ultrafiltration [15], enzymeimmobilization [16] , and pervaporation[17] .

2. Materials and Methods

Acrylonitrile (AN) (BDH chemicals, LTD ,England) stabilized with 0.1 % Hydroquinone, was washed with Sodium hydroxide solution to remove inhibitor. The crude AN monomer was degassed

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and twice distilled on a vacuum line, dried over anhydrous Na_2SO_4 and stored below -18 ^{0}C.

The Khulays bentonite was kindly supply by Saudi Geological Survey (SGS) (Saudi Arabia, Jeddah). Exchanged treated clay was prepared [10] by ion-exchanged method using solutions of $Al(SO_4)_3.16H_2O$. The exchanged clay was repeatedly washed and centrifuged before drying in a oven at 60 ^{0}C for several days. It was then ground and sieved at 106 mesh (ASTM). The material was then stored in a dry-air container.

Potassium persulphate ($K_2S_2O_8$), methanol, acetic acid and DMSO were products of BDH chemicals LTD. .

2.1. Thermal Analysis

Thermogravimetry (TG) was recorded for polymer using Mettler 3000 TA thermobalance. The sample (about 10 mg) at heating rate of 10 ^{0}C /min in air media. The TGA experiment was taken over a temperature range 30–800 ^{0}C.

Differential scanning calorimetry (DSC). Analysis was conducted by a DSC-30 unit of the Mettler TA-3000 system. The DSC analysis at a heating rate of 10 ^{0}C /min from 50 to 500 ^{0}C; plot 10 cm; and full-scale range, 25 mW .

2.2. Polymerization of acrylonitrile (AN) in presence of treated Khulays bentonite

The polymerization experiments were placed in the reaction vessel containing known concentrations of initiator and the monomer acrylonitrile (AN). The exchanged Khulays bentonite was added and then the flask was well stoppered and and maintained at the desired temperature by a thermostat. The requisite

amount of the initiator solution was carefully added to the reaction mixture. The reaction was stopped by keeping the flask in ice-cold water and by addition of a known excess of hydroquinone, which spontaneously consumed the unreacted free radicals. The precipitated polymers were filtered and purified by washing repeatedly with distilled water and absolute alcohol. Then they were dried till a constant weight at about 60 ^{0}C. The percentage conversation was determined gravimetrically.

3. Results and Discussion
3.1. Catalytic Studies
3.1.1. The effect of time on polymerization

The effect of polymerization temperature is illustrated in Figs. 1, keeping the concentrations of AN, $K_2S_2O_8$ and catalyst weight constant at 1.518, 0.03 mol.dm^{-3} and 0.5 g, respectively The polymerization conversion increased sharply increase in the polymerization temperature from 40 to 70 ^{0}C in the conversion in the first step of the polymerization process. After that sharp increase there is an additional moderate increase in the conversion. Finally, there is no further change, indicating the end of the polymerization process which may be due to chain termination processes predominate, leading to deactivation of the catalyst. Similar general behavior of the polymerization efficiency as a function of time was previously reported [18-20].

3.1.2. The effect of monomer concentration

The effect of monomer concentration in the polymerization was investigated in the range (1.137- 4.171 mol.dm^{-3}) at a fixed concentration of
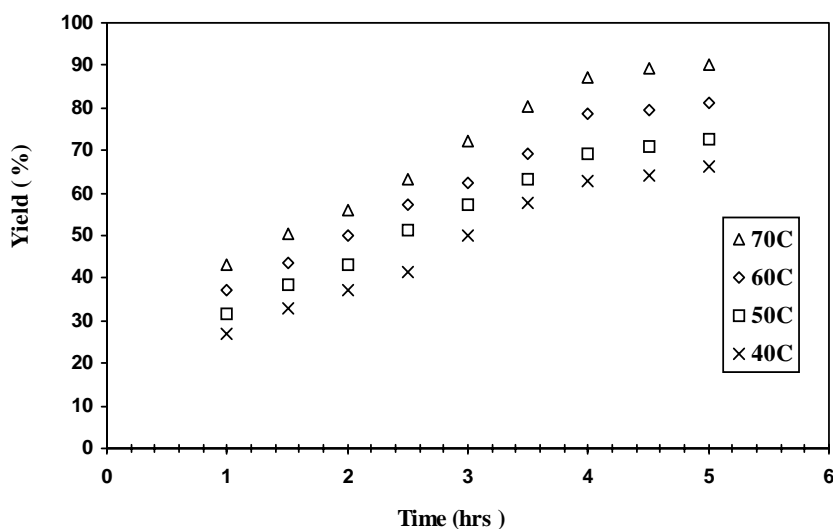
Figure 1. The effect of reaction time on the polymerization of acrylonitrile: Reaction condition: 0.5 g exchanged bentonite; acrylonitrile 1.886 mol.dm^{-3}; $K_2S_2O_8$ 0.03 mol.dm^{-3} at different temperature

Table 1. The effect of concentration of AN, $K_2S_2O_8$ and bentonite weight on the conversion of polymerization of acrylonitrile at 60 ^{0}C for 3h.

AN (mol.dm^{-3})	$K_2S_2O_8$ (mol.dm^{-3})	Catalyst weight (g)	Conversion (%)
1.137	0.03	0.50	75.7
1.886	0.03	0.50	83.6
2.645	0.03	0.50	88.2
3.412	0.03	0.50	82.3
4.171	0.03	0.50	71.6
1.886	0.01	0.50	43.1
1.886	0.02	0.50	60.4
1.886	0.03	0.50	75.7
1.886	0.04	0.50	79.9
1.886	0.05	0.50	82.3
1.886	0.03	0.10	40.4
1.886	0.03	0.25	59.7
1.886	0.03	0.50	75.7
1.886	0.03	0.75	77.4
1.886	0.03	1.00	72.7
1.886	0.03	1.25	70.2
1.886	0.03	1.50	67.5

the other reagents at 60 ^{0}C. The results obtained are shown in (Table 1). With increase in monomer concentration up to 2.645 mol.dm^{-3}, the conversion increase and then decrease. As can be expected, increasing the AN concentration may increase the polymerization rate, and thus increase the precipitation rate of the oligomeric chains. The decrease of conversion may be due to an increase in the viscosity of the medium and a consequent decrease in the mobility of propagating species [21-22] .

3.1.3. Effect of $K_2S_2O_8$ concentration

The effects the conversion have been studied by varying the concentration of the initiator in the range 0.01-0.04 mol.dm^{-3} by keeping the con-

centrations of the other reagents fixed at 60 ^{0}C. as given in Table 1. With the increase in $K_2S_2O_8$ concentration in the above range the conversion were found to increase due to an increase in concentration of the active species [23] resulting in smaller oligomers with higher critical micelle concentration (CMC). Increasing the initiator concentration causes an increase in the oligomeric radicals' concentration, and thus in the number of PAN chains. This may lead to an increase in the number of PAN (more nuclei) and an increase (more PAN chains participating in the growing process). Moreover, a higher initiator concentration increases the growth rate of the oligomeric chains [24-25] . Initiator by using the concentrations of AN, $K_2S_2O_8$ and catalyst weight constant at 1.518, 0.03 mol.dm^{-3} and 0.5 g at 60 ^{0}C. The reaction was carried out in various solvents like water ,methanol, acetic acid and DMSO. The results obtained in the order: water >methanol >acetic acid> DMSO. The results were shown in (Fig. 2). It was found that the [DMSO] has no effect on the rate of polymerization. The retardation by the solvents may by due to: (i) the oxidation of the additives by $K_2S_2O_8$, thus reducing the optimum concentration of the initiating radicals in the immediate vicinity of the monomer, (ii) the premature termination resulting from activity transfer to these solvents [26-27] .

3.1.4. Activation Energy of polymerization

Apparent activation energy, Ea was calculated from initial rate of polymerization of AN with treated clay, at 55, 60, 65 and 70 ^{0}C. Plots of ln K vs. 1/T were made so the activation energies could be determined by using Arrhenius
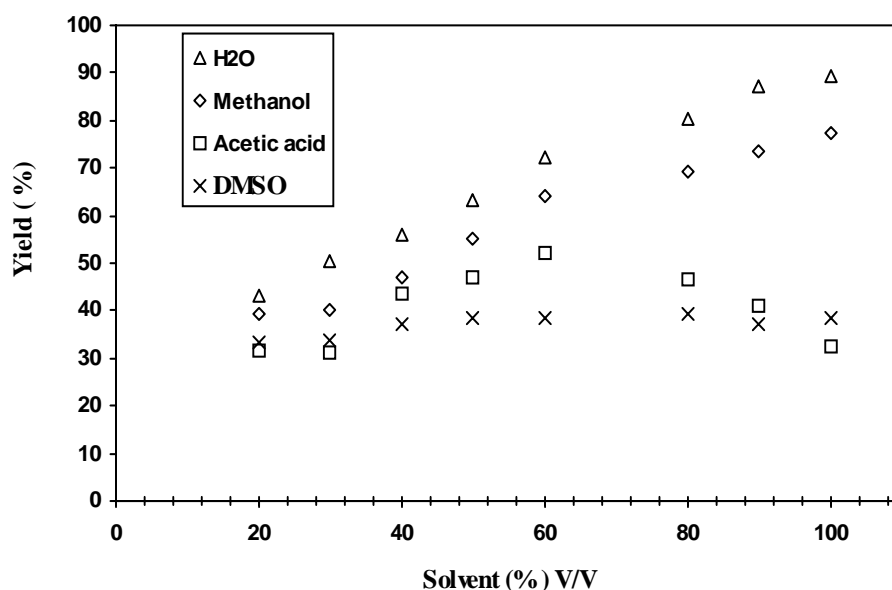
Figure 2. The effect of different solvent on the polymerization of acrylonitrile: Reaction condition: 0.5 g exchanged bentonite); acrylonitrile 1.886 mol.dm^{-3}; $K_2S_2O_8$ 0.03 mol.dm^{-3} at temperature 60 ^{0}C

relationship. Table (2) represents the activation energy of polymerization of AN.

**Table 2.** Activation Energies of Polymerization of acrylonitrile with AN.

$K_2S_2O_8$ concentration (mol/l)	Activation Energies Ea (kJ/mol)	
	ANC only	ANC +Bentonite
0.01	42.5	37.3
0.02	35.4	31.1
0.03	28.3	22.1
0.04	24.2	17.3

3.2. Thermal study of PAN

Figure 3 represents the TG and DTG curve for the polyacrylonitrile (PAN). The DTG analysis shows three steps thermal degradation processes, the first step weight loss occurs in the temperature range 73–182 ^{0}C with a mass loss of 8.25 % which is due to expulsion of loosely bounded water molecule from the polymer chain [28-29].The second step weight loss occurs in the temperature range 220–309 ^{0}C with a weight loss of 7.7% which can be attributed to the loss of oligomers. The third and final step weight loss occurs in the temperature range 317–582 ^{0}C with a mass loss of 60.5 %. Followed by degradation at higher temperature the strong dipole-dipole interaction between the polymer networks may be the prime reason for higher thermal stability of PAN [30]. The total weight loss in air up to 800 ^{0}C about 90%. DSC curve is shown in Figure 2 .The DSC thermograms show that AN polymer exhibits a sharp exothermic cyclization peak at 288 ^{0}C .This exothermic is related to the cyclization reaction of nitrile groups [31].
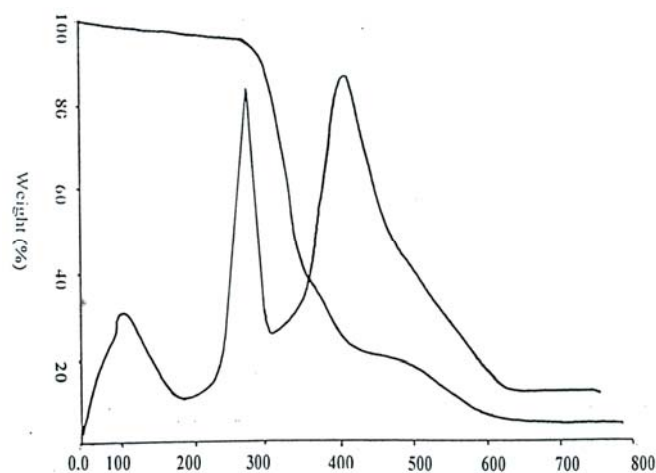
Figure 3. TGA and DTGA thermogram of poly-acrylonitrile (PAN)
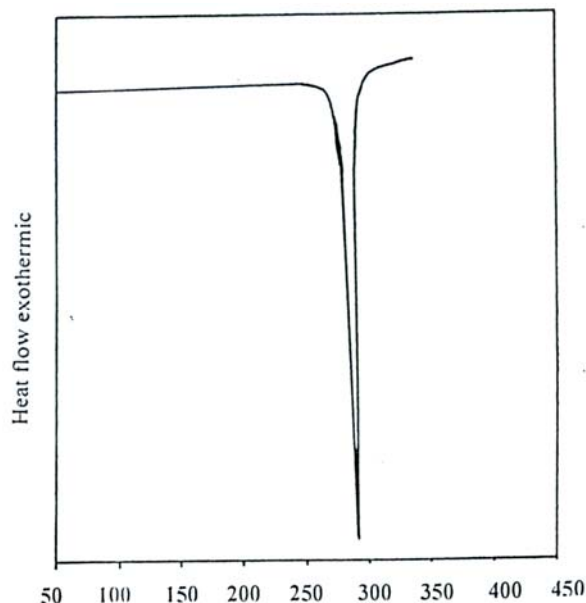
Figure 4. DSC thermogram of polyacrylonitrile (PAN)

4. Conclusions

The khulays bentonite catalyzed aqueous polymerization of acrylonitrile (AN) has been significantly carried out and factors affecting the polymerization have been investigated. The advantages of using this catalyst are: (i) use of cheap and easily available catalyst, (ii) requirement of small amount of catalyst, (iii) short reaction times, (iv) high product yields. Thermal properties of the polymer were studied by TGA and DSC techniques.

References

[1] Milliken, T.K, Miles, G.A, and Oblad. A.D., Trans.,Faraday Soc., 8, 50, 279.
[2] Pinnavaia, T.J. , Tzou, M.S. , Landau, S.D. , Raythatha, R.H. , J. Mol. Catal. 27 (1984) 195.
[3] Yoo, J.W., Lee, C.W., Jeong, H.-C. , Park, Y.-K. , Park, S.-E. , Catal. Today, 60 (2000) 255.
[4] Choudary, B.M. , Kantam, M.L., Sateesh, M. , Rao, K.K. , Santhi, P.L., Appl. Catal. A: Gen. , 149 (1997) 257.
[5] Inui, K. , Kurabayashi, T., Sato,S., Ichikawa, N., J. Mol Catal. A , 216 (2006), 147.
[6] Laszlo, P., and Mathy, A., Hev.Chim.Acta, 70, 1987, 577.

[7] Vinu, A., Ariga, K., Devassy, B.M., M. Hartmann, Halligudi, S.B., Micropor. Mesopor. Mater. 80 (2005) 195.

[8] Al-Esaimi, M.M., Inter Jour. Chem., 16, 2006, 75.

[9] Cornelis, A., Laszlo, P, and Pennelneau, P., Bull. Soc. Chim, BELG., 961, 1987, 29.

[10] Al-Esaimi, M.M., J. Appl. Polym. Sci., 64, 1997, 367.

[11] Breen, C., Zahoor, F., Madejova, D., Komadel, P.J., J. Phys. Chem. B, 101, 1997, 5324.

[12] Eliseeva VI. Emulsion polymerization and its application in industry. New York : C Bureau, 1981.

[13] Kotkar, D., Ghosh, P.K., J. Chem. Soc. Chem. Commun., 950, 1986.

[14](a) Lin WC, Liu TY, Yang MC. Biomaterials, 25, 2004, 1947.
(b) Clark WR, Gao D, Ronco C. In: Ronco C, La Greca G, editors., Hemodialysis technology. Basel: Karger Publisher; 2002. p. 70.

[15](a) Ulbricht M, Richau K, Kamusewitz H.,Colloid Surf ,A,138,1998, 353.
(b) Musale DA, Kulkarni SS. J Membr Sci 1997, 13,136.
(c) Qin JJ, Cao YM, Li YQ, Li Y, Oo MH, Lee H. Sep Purif .Technol, 36, 2004, 149.
(d) Jung B. J Membr. Sci, 129, 2004,229.
(e) Yang MC, Liu TY. J Membr. Sci., 119,2003,226.

[16] (a) Ulbricht M, Papra A. Enzyme Microb .Technol, 199761.
(b) Godjevargova T, Konsulov V, Dimov A. J Membr. Sci,152,1999,235.
(c) Godjevargova T, Dimov A, Vassileva N. J Membr. Sci, 116, 1996,273

[17](a) Bhat AA, Pangarkar VG. J Membr. Sci, 167, 2000, 187.
(b) Mandal S, Pangarkar VG. Sep Purif .Technol, 30, 2003,147.

[18] Shen,S., Sudol,E.D., El-Aasser,M.S., J. Polym. Sci. Polym. Chem. 31,

[19] Liu, J., Chew, C.H., Wong, S.Y., Gan, L.M. , Lin, J. ,Tan, K.L. , Polymer 39 (1998) 283.

[20] Capek, I. , Macromol. Chem. Phys. 195 (1994) 1137.

[21] Christian, P., Giles, M.R., Griffiths, R.M.T.,Irvine, D.J., Major, , D.J., S.M. Howdle, Macromolecules 33 (2000) 9222.

[22] Shen,S., Sudol, E.D., El-Aasser, M.S., J. Polym. Sci. Polym. Chem. 30 (1992) 2765.

[23] Beharai,K.,Bahadur,L.,Agarwal,U., J. Am. Chem. Soc., (Polym.Div.) Polym.Prep., 35,1994, (1)117.

[24] Capek, I., Le Quang, T. , Makromol. Chem. 187 (1986) 2063.

[25] Candau,F., Ottewill,.H.,R "An Introduction to Polymer Colloids", Kluwer Academic, Dordrecht, 1990.

[26] Wang YM, Feng LX, Pan CY. J Appl Polym Sci,70,1998,2307.

[27] Huang X, Brittain WJ. Macromolecules , 34,2001, 3255.

[28] Khor,S.H., Neoh,K.G., Kang,E.T., J. Appl. Polym. Sci., 40, (1990), 2015.

[29] Yue,J., Epstein,A.J., Zhong,Z., Gallagher,P.K., Mac Diarmid,A.G.,

[30] Freshour,G.B., in: Masson,J.C. (Ed.), "Acrylic Fibre Technology and Applications", vol. 1, Marcel Dekker, New York, 1995, Chapter 7, p. 197.

[31] Lin W, Hsieh YL, Warganich D, Zhou WJ, Kurth MJ, Krochta M., Polymer, 39, 1998,4911.