

Emulsifier-Free Emulsion Polymerization of Styrene

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ABSTRACT: Polystyrene latex particles in an emulsifier-free emulsion were prepared by purified styrene (St) as monomer and 2,2'-azobis (2-amidino propane) dihydrochloride (ABA, 2HCl) as initiator. The optimized condition of polymerization of styrene was obtained by using the various parameters such as different amounts of monomer (0.009, 0.051, and 0.071 mol styrene/mol Water), different amounts of initiator (6.02, 4.62, 2.41, and 1.00 weight percent of initiator relative to styrene), and pH (range 1–7). Quantitative and qualitative analyses of prepared polymer were per-

formed by Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC), and ¹H-NMR and FT-IR spectroscopy, that were used, respectively, to show the morphology of particles, the glass transition temperature (T_g), the average molecular weight, and the structure of the prepared polymer. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1898–1904, 2004

Key words: styrene; ABA, 2HCl; emulsifier-free emulsion; SEM; DSC; GPC

INTRODUCTION

Emulsion is a disperse system, which in general terms contains two insoluble or slightly soluble phases.¹ One of the main components in emulsions is the emulsifier. Selection of the emulsifier has an important role in preparation of a suitable and stable emulsion.²

Emulsions are also divided into four categories according to the size of the dispersed phase: (1) macro emulsion, (2) micro emulsion, (3) colloid, and (4) latex.³ The other type of emulsion polymerization is emulsifier-free emulsion polymerization. Since 1965, when Matsumoto and Ochio⁴ first proposed that the monodisperse microsphere could be prepared by an emulsifier-free emulsion polymerization, based on a styrene/potassium persulfate/water (St/KPs/H₂O) system, the technique has become of significant interest.

This system is a technique derived from conventional emulsion polymerization in which polymerization is carried out in the absence of emulsifiers. This technique has been extraordinarily useful for the preparation of model polymer colloids with narrow particle size distributions and well-characterized surface properties. This system gains colloidal stability via the involvement of one of the following reactive components that acts as an emulsifier: (1) ionizable initiator, such as potassium persulfate^{5,6} and azobis(isobutyramidine hydrochloride)⁷; (2) hydrophilic comonomers,

such as carboxylic monomers,⁸ acrylamide, and its derivatives^{9,10}; and (3) ionic comonomers, such as sodium styrene sulfonate and the sodium salt of 2-sulfoethyl methacrylate (NaSEM).¹¹

Another important property for this type of latex is its low polydispersity, a small size compared with one obtained by conventional emulsion polymerization.¹²

Latex systems with controlled particle morphology are the basis for many of today's advanced high performance polymer materials, which are extensively used in a wide variety of industries, ranging from coatings and adhesives to biomedical and biotechnology. Extensive studies have been carried out on the morphology of the submicron size composite latex particles prepared by two-stage emulsion polymerization, ranging from Core-shell to various fragmented inclusions to inverted Core-Shell.^{13,14}

It was shown that the emulsifier-free polymerization of methacrylate initiated by 4,4'-azobis (4-cyanovaleric acid) at high initial pH values differs from the polymerization of styrene carried out under analogous conditions,¹⁵ and also narrowly distributed emulsifier-free cationic polymethylacrylate latex particles were prepared by using microwave irradiation in the presence of initiator 2,2'-azobisisobutyramidine dihydrochloride.¹⁶

In this work, the optimized condition of polymerization of styrene was obtained using the various parameters such as different amounts of monomer, different amounts of initiator, and pH; and 2,2'-azobisisobutyramidine dihydrochloride (ABA, 2HCl) was chosen as initiator. This is a water-soluble initiator decomposing to two positively charged radicals,

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TABLE I
The Optimized Conditions for Preparation of PS

Styrene (mL)	Distilled water (mL)	Initiator (gr)	Temperature (°C)	pH	Speed (rpm)
5.5	100	0.23	70	7	320

TABLE II
Effect of pH in Constant Ratio of St/H₂O (11.6 : 26)

Exp. No.	St (mL)	H ₂ O (mL)	Initiator (gr)	Time (hr)	Temperature (°C)	PH	Speed (rpm)
1	11.6	26	0.3	5	70	7	320
2	11.6	26	0.3	5	70	4-5	320
3	11.6	26	0.3	2.5	70	1-2	320

which will start the polymerization in the aqueous phase.

EXPERIMENTAL

Materials

The used styrene was supplied by Merck Chemical Co. (Whitehouse Station NJ). It was purified by distillation under vacuum (0.5% CuI was used for preventing polymerization of styrene) and was stored in a dark bottle at -20°C until required.

The initiator was 2,2'-azobisisobutyramidine dihydrochloride that was supplied by Wako Chemical Company (Richmond, VA) as V-50. It was kept at 4°C and was used without further purification.

Distilled water and hydrochloride acid had control of pH in all of the polymerization reaction.

Equipment

The samples were characterized by Scanning Electron Microscopy (ZEISS DSM 960A, Oberkochen, Ger-

many) and Differential Scanning Calorimetry (PL DSC, England). GPC analysis was performed by using water 150C HPLC/GPC.

Sample preparation

For SEM analysis, the emulsion samples were diluted by water 1 : 1000(v/v). A drop of the dilute emulsion was placed on the sample holder and was dried under freeze-drying. They were then placed under vacuum, flushed with Ar, evacuated, and coated with powdered gold.

The obtained latex was used for GPC analysis after drying at 60°C under vacuum. The mobile phase was DiMethylFormamide (DMF) with flow rate of $1\text{ mL}\cdot\text{min}^{-1}$ in the period of 40 min. GPC data were recorded at 70°C on an ultrastyrogel column equipped with RI detector.

Polymerization

The optimized conditions for preparation of PS via emulsifier-free emulsion polymerization are given in Table I.

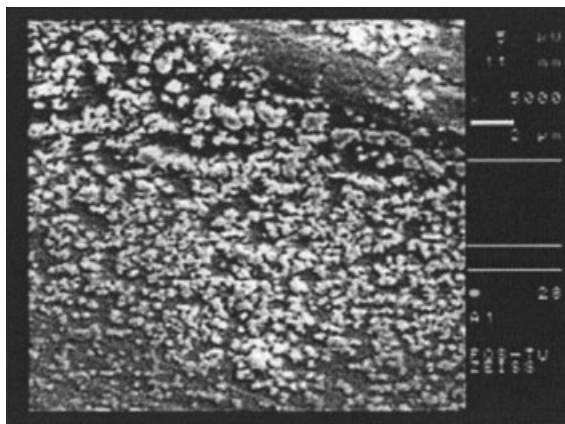


Figure 1 SEM micrograph of PS from experiments No. 1 and 2.

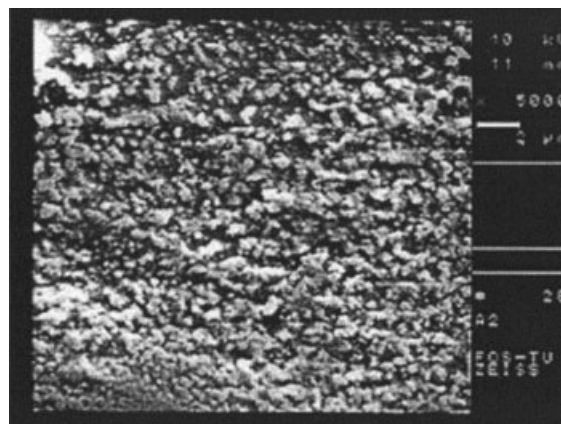


Figure 2 SEM micrograph of PS from experiment No. 3.

TABLE III
Effect of Different Amounts of Monomer

Exp. No.	St (mL)	H ₂ O (mL)	Initiator (gr)	Time (hr)	Temperature (°C)	PH	Speed (rpm)
1	11.6	26	0.3	5	70	7	320
4	11.6	36	0.3	5	70	7	320
5	5.5	70	0.3	24	70	7	320
6	5.5	100	0.3	24	70	7	320
7	5.5	130	0.3	24	70	7	320

The polymerization reactions were carried out in a 150 mL round-bottomed flask with a three-necked flanged top.

A typical preparation is as follows:

90 mL of distilled water was added to the flask. A Teflon stirrer with half-moon shape was connected to a stainless steel shaft fitted with a Teflon guide and was added to the central outlet of the flask cover. The shaft was connected to a digital motor, which indicated the agitator speed. The water-cooled reflux condenser was added to the second outlet of the flask.

The flask was immersed in a thermostat water bath. A thermometer was placed in the water bath ($70 \pm 0.5^\circ\text{C}$).

A nitrogen gas blanket was maintained over the reacting medium throughout the reaction. After stirring for 15 min, under nitrogen atmosphere, 5.5 mL of styrene was added to the reactor. The system was then left for 15 min to attain temperature equilibrium. The initiator was dissolved in 10 mL of water. A reaction time of 24 h was found to be adequate, although this depended on the experimental conditions.

The purpose of the present work is to explore the polymerization conditions to obtain the 40% solid contents.

RESULTS AND DISCUSSION

The optimized condition of polymerization of styrene via emulsifier-free emulsion polymerization was ob-

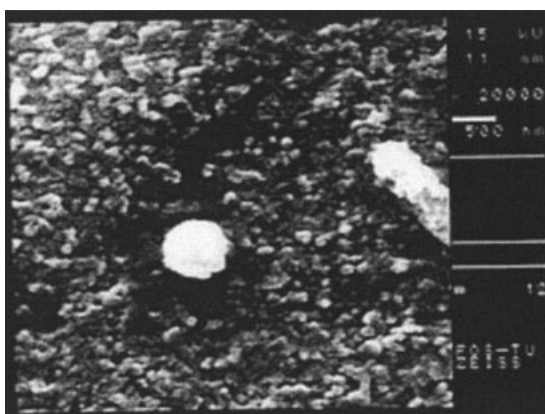


Figure 3 SEM micrograph of PS from experiment No. 5 (reaction time = 4 h).

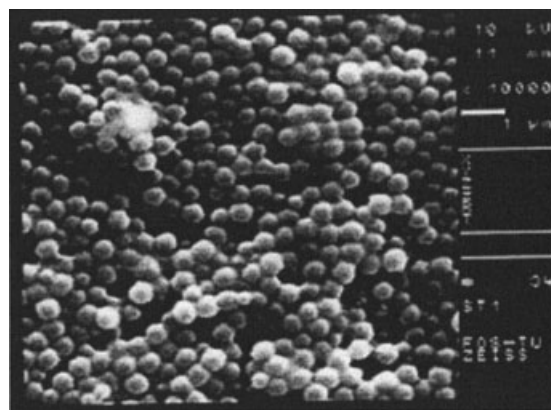


Figure 5 SEM micrograph of PS from experiment No. 6.

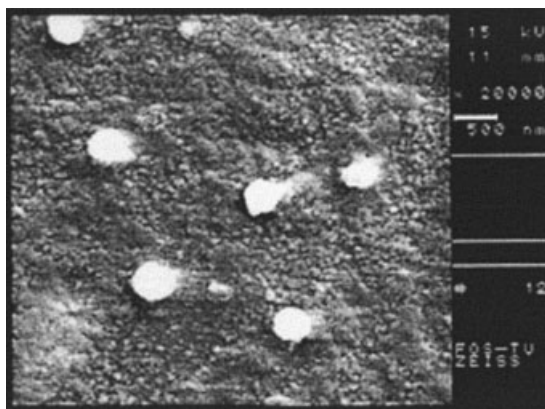


Figure 4 SEM micrograph of PS from experiment No. 5 (reaction time = 24 h).

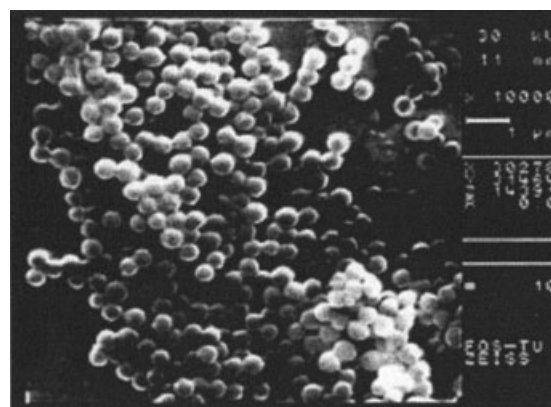


Figure 6 SEM micrograph of PS from experiment No. 7.

TABLE IV
Effect of pH, in Constant Ratio of St/H₂O (1 : 18.18)

Exp. No.	St (mL)	H ₂ O (mL)	Initiator (gr)	Time (hr)	Temperature (°C)	PH	Speed (rpm)
8	5.5	100	0.23	24	70	7	320
9	5.5	100	0.23	24	70	4-5	320
10	5.5	100	0.23	2.5	70	1-2	320

tained by examination of various parameters such as pH, monomer concentration, and initiator concentration.

Effect of pH

In Table II the effect of pH, in the ratio 11.6 : 26 mL St and mL H₂O, respectively, is shown.

In experiments No. 1 and 2 that are carried out at pH = 7 and pH = 4-5, respectively, the whole system coagulated after 5 h.

In experiment No. 3 that is carried out at pH = 1-2, the whole system coagulated after 2.5 h.

These experiences show that the emulsion system in all experiences is not stable, but the above results indicate that the emulsion system in pH = 7 is more stable than in pH = 1-2 due to the fact that the emulsion system is not stable in low pH.

Figures 1 and 2 are the SEM micrographs of the PS particles that have been obtained from experiments No. 1 and 2, and experiment No. 3, respectively.

These figures show the coagulated and amorphous particles that have been formed in over emulsion polymerization.

Effect of different amounts of monomer

In Table III, the effect of different amounts of monomer is shown. In the first two experiments, the whole emulsion system coagulated after 5 h.

Figures 3 and 4 show the SEM micrographs of the PS particles that were formed in experiment No. 5. In this case, after 24 h, the latex system got very stable with reaction yield (Ra) 15%, but a small amount of emulsion was coagulated. Figure 5 shows the SEM micrograph of the spherical PS particles that were obtained from experiment No. 6; their size is about 300-400 nm, and the emulsion system is very stable with reaction yield (Ra) 40%.

PS spherical particles that are formed from experiment No. 6 show a more stable emulsion system than experiment No. 5, and also reaction yield has been increased in experiment No. 6. The amount of monomer has been decreased in experiment No. 7 rather than No. 6, but the stability of the system and the reaction yield are not changed. The micrograph of PS particles in experiment No. 7 is shown in Figure 6.

The above results indicate that decreasing monomer concentration in pH = 7 increases the stability of the latex, and the best conditions are shown in experiment No. 6.

Effect of pH

As shown in Table IV, the effect of pH, in constant ratio of St/H₂O (1 : 18.18), is examined.

In experiments No. 8 and 9, after 24 h in pH = 7 and 4-5, respectively, the latex system was very stable and reaction yield was 39% in both experiments; but in experiment No. 10, after 2.5 h in pH = 1-2, the whole emulsion coagulated. Thus, it is found that the stability of latex decreases very much in more acidic conditions.

The micrograph of the PS particles formed in experiment No. 8 is shown in Figure 7.

Effect of different amounts of initiator

Table V shows the effect of different amounts of the initiator in the optimized condition of emulsifier-free emulsion polymerization of St.

In all experiments that are mentioned in Table V, the latex is very stable over reaction time. Figure 8 shows the PS spherical particles that were obtained from experiment No. 11.

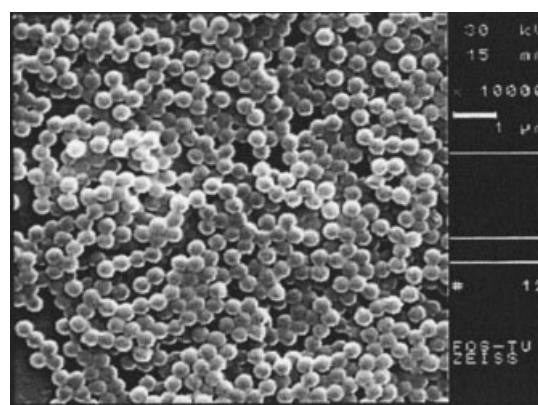


Figure 7 SEM micrograph of PS from experiment No. 8.

TABLE V
Effect of Different Amounts of the Initiator

Exp. No.	St (mL)	H ₂ O (mL)	Initiator (gr)	Time (hr)	Temperature (°C)	PH	Ra %	Speed (rpm)
6	5.5	100	0.30	24	70	7	40	320
8	5.5	100	0.23	24	70	7	39	320
11	5.5	100	0.12	24	70	7	20	320
12	5.5	100	0.05	24	70	7	15	320

As shown in Table V, increasing the amount of initiator increases the reaction yield. This is due to the number of active sites in particles, which will increase.

The weight percent of the initiator relative to monomer and the reaction yield are 6.02 and 40%, respectively, in experiment No. 6; in experiment No. 8, those are 4.62 and 39%. It is found that if weight percent of the initiator increases from 4.62% to 6.02%, the reaction yield will increase only 1.40%. On the other hand, this increase does not have a high influence on the reaction yield, so

experiment No. 8 has optimized conditions for emulsion-free emulsion polymerization of styrene.

SEM, GPC, DSC, ¹H-NMR, and FT-IR spectroscopy performed characterization of PS prepared from experiment No. 8.

DSC analysis of PS obtained from experiment No. 8 (Fig. 9) shows a peak at 110°C that is the glass transition temperature (T_g) of PS. Number average molecular weight (M_n) of PS, determined by GPC in Figure 10, was 10,896 and its weight average molecular weight (M_w) was 273,085 with molecular weight distribution of 25.

The GPC chromatogram shows a bimodal curve that corresponds to two different types of molecular weights of PS, and high polydispersity may be the result of the presence of oligomers with low molecular weight, shown as a small curve at the end of the chromatogram. FT-IR and ¹H-NMR show the structure of the prepared polymer (Figs. 11 and 12, respectively). The results are as follows:

FT-IR (KBr): C-C stretching vibration of benzene ring and C-H asymmetric bending vibration of CH₂ and CH₃ of polystyrene are 1598.9, 1490.8 (cm⁻¹), and 1448.4 (cm⁻¹), respectively. ¹H-NMR: The chemical shifts of aliphatic and aromatic protons of polystyrene,

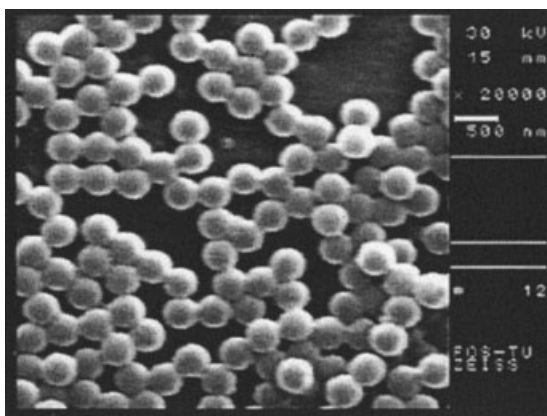


Figure 8 SEM micrograph of PS from experiment No. 11.

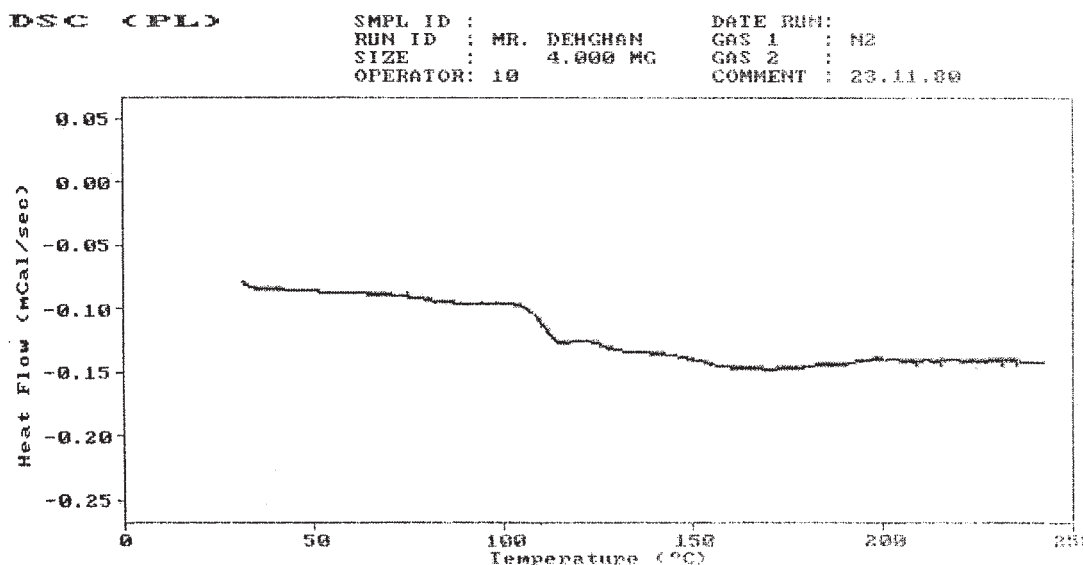


Figure 9 DSC trace of the polymer from experiment No. 8.

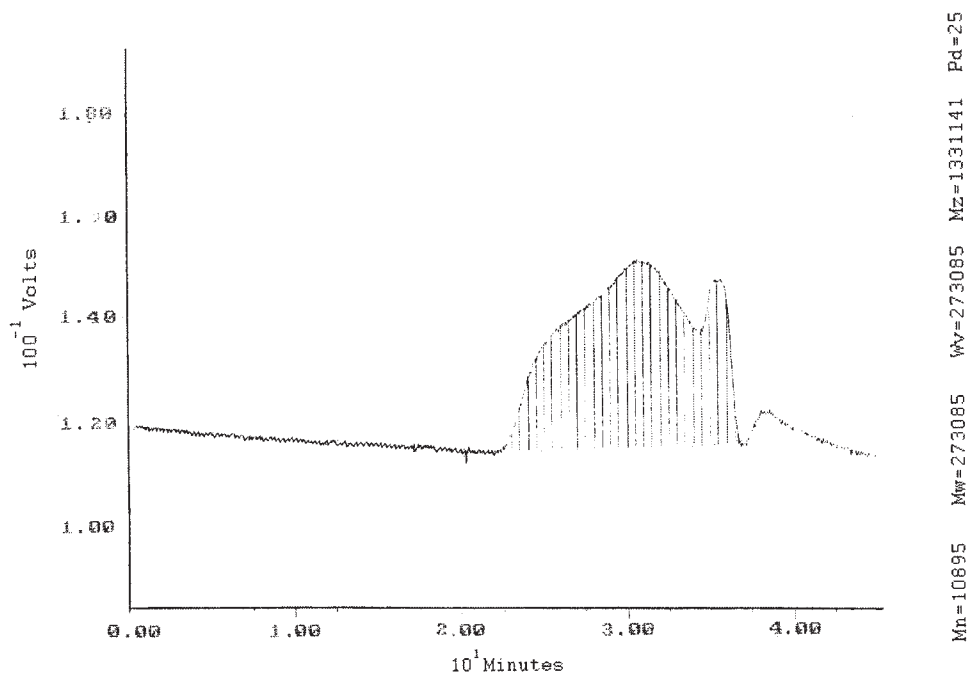


Figure 10 GPC analysis of the polymer from experiment No. 8.

in CDCl_3 solvent, are 1.5 (ppm) and 7.2, 7.3, and 6.5 (ppm), respectively.

CONCLUSION

The procedure presented here results in the preparation of polymer particles of styrene via emulsifier-free

emulsion polymerization, and ABA, 2HCl plays the role of the initiator and the emulsifier in this method.

Stability of the latex system in this procedure was affected by important parameters such as different amounts of monomer and pH.

PS spherical particles in the size of about 300–400 nm can be obtained by this method.

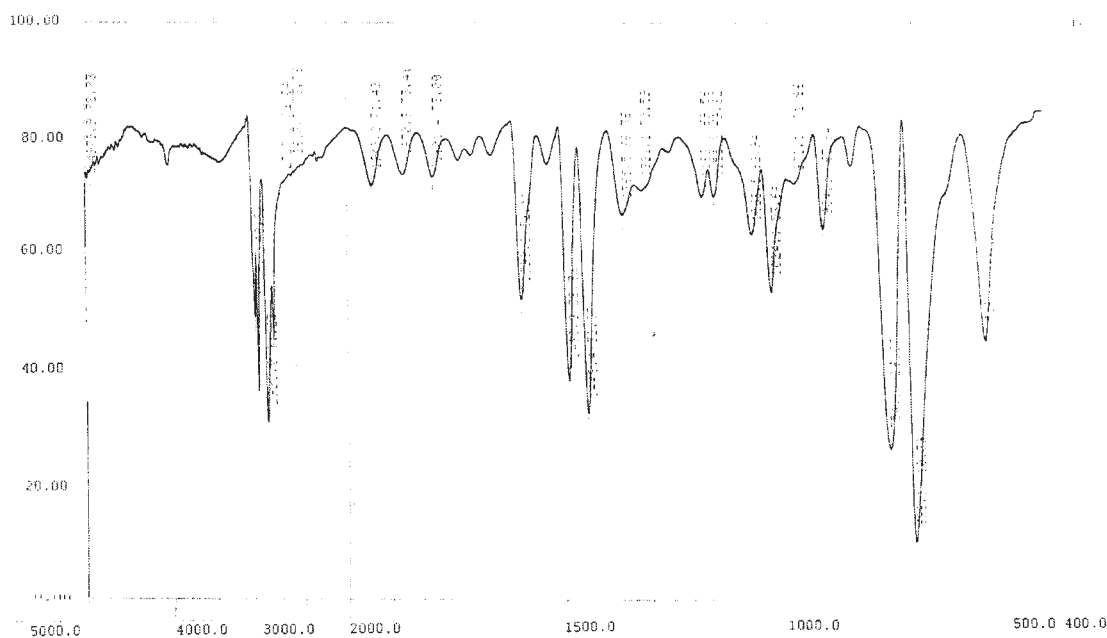


Figure 11 FT-IR of the polymer from experiment No. 8.

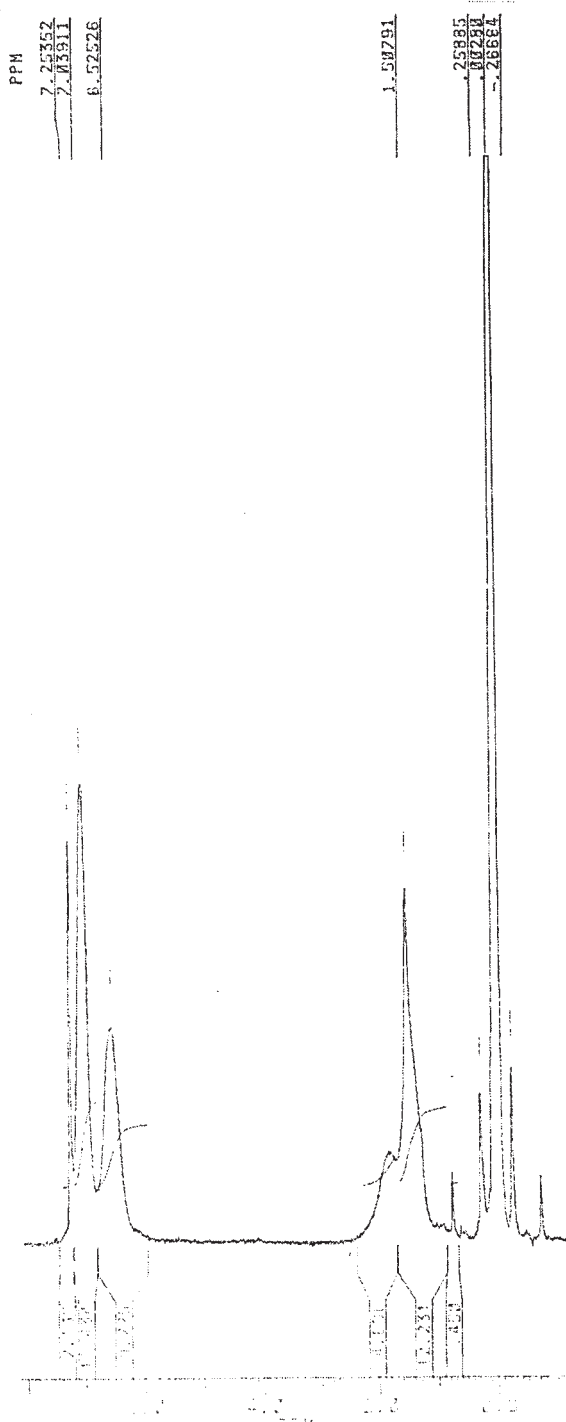


Figure 12 $^1\text{H-NMR}$ of the polymer from experiment No. 8.

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