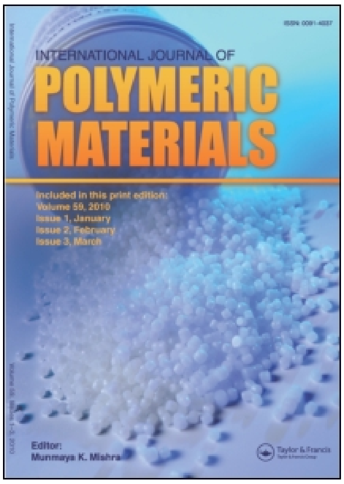

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Liquid hydrocarbon-absorbents, 1: Preparation and evaluation of styrenic absorbents for liquid aromatic hydrocarbons

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LIQUID HYDROCARBON-ABSORBENTS, 1: PREPARATION AND EVALUATION OF STYRENIC ABSORBENTS FOR LIQUID AROMATIC HYDROCARBONS

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Bulk, Solution, and suspension methods were used to radically polymerize styrene/ethyleneglycol dimethacrylate for obtaining liquid aromatic hydrocarbon-absorbing materials. The polymerizations initiated by benzoylperoxide or azobis(isobutyronitrile), were performed under atmospheric conditions. Variety of suspending agents were used and evaluated in order to optimize particle size and shape with the suspension technique. Advantages and disadvantages of the individual techniques were reported for styrene polymerization in the presence of ethyleneglycol dimethacrylate as a crosslinking agent. Products were evaluated in terms of their swelling capacity in toluene. Products of medium to high absorbency as well as of good gel strength were obtained.

Keywords: hydrocarbon absorbent, styrene, polymerization, swelling

INTRODUCTION

The main driving force for working on the preparation of absorptive materials for organic liquids has been the environmental pollution caused by oil-spills [1–3]. Its damage is tremendous and lasts for long periods of time. On the occurrence of an oil-spill event or organic-spill from chemical industries, many attempts have been made to get rid of the liquids [4]. Natural cleaning, allowing oil to be degraded and removed by natural means [5], takes long time to be fully effective. This method can be enhanced by an oil dispersing or an oil sinking agent. Oil gelling agents act as surface-tension modifiers, coagulating the spilled oil [6], and enhancing the potential for mechanical removal techniques [7], e.g., recovery of the solidified oil with a net. In both cases, there is a disadvantage in that the spilled oil cannot be recovered. Therefore, recent attempts have been focused on oil absorbents

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[4, 6 – 8]. For this purpose, polypropylene fiber or non-woven fabrics, melt-blown polyesters and polyurethane foam sheets have already been used. Shimizu et al. [9], have designed an oil-recovery machine to overcome some disadvantages regarding the bulkiness and inconvenient shipping and storage of the absorbents.

Another important aspect of the organic-absorbent is related to fuel absorbency that may be used to prepare solid fuels or to control fuel evaporation loss in automobile canisters or boiler fuel tanks [10].

The present project had been done as a part of larger work on the preparative practical methods for obtaining absorbents for liquid hydrocarbons. This paper deals with some trials on the synthesis of styrene-based gels for absorbing toluene as a representative of the liquid aromatic hydrocarbons.

EXPERIMENTAL

Technical-grade styrene monomer and toluene (Tabriz Petrochemical Complex, Tabriz, Iran) were used as received. Ethyleneglycol dimethacrylate (EGDM, Fluka) was used without further purification. All the suspending agents including poly(vinyl alcohol) were purchased from Aldrich. Dibenzoyl peroxide (BPO, Merck, containing 25 Wt.% of water) and azobis(isobutyronitrile) (AIBN, Merck) were also used as supplied.

Synthesis

Bulk, solution and suspension polymerization techniques were examined to achieve the most practical procedure. All reactions were performed non-isothermally with a fixed bath (starting) temperature, under atmospheric conditions.

Bulk and Solution Polymerization

A 250-ml vessel equipped with a condenser and mechanical stirrer was charged with the reactants (styrene, EGDM, BPO) and the solvent (if any). The vessel was immersed in a thermostatic water- or silicone oil-bath, adjusted at a given temperature. In bulk cases, no changes were observed during the early minutes (5 – 15 min.) of the reaction, due to a retardation period. This period was expanded to 50 – 60 min. in case of solution polymerizations. After this period, the mixture became viscous and a few minutes later, gelation occurred. Stirring was ineffective because of the high reaction mixture viscosity. The mixture was allowed to heat up at the given bath temperature for an additional 10 min. The main disadvantages of these both methods are related to a few non-practical time-consuming work-up steps that must be done. The rubber-like mass (in the bulk method) and the swollen gel (in the solution method) should be cut into small pieces and then poured into a large volume methanol and stirred overnight. The turbid supernatant was decanted. Fresh methanol was added and the vessel was allowed to stand overnight to complete the removal of all the residual monomers and impurities from the polymer particles. The white particles were filtered, dried out at room temperature (for 18 hr.) and then at 70°C in a forced draft oven for 6 hr. A hammer-type minigrinder was used to grind the particles (frozen with liquid N_2) into 40 – 60 mesh in size.

Suspension Polymerization

A 250-ml reaction vessel equipped with a propeller stirrer, condenser and dropping funnel, was charged with distilled water as well as suspending agent(s) and placed into a thermostatic water bath at 80°C. No provisions were made to exclude air. The stirring rate was adjusted at 400 rpm. The preheated organic phase components (styrene, EGDM, BPO) was added dropwise (one drop per second) to the aqueous phase through dropping funnel. The dispersed tiny organic droplets became sticky just after 3 – 4 h (retardation time). Stirring stopped only when the dispersed droplets had hardened without affinity to stick together (about 5 – 8 h). The mixture was cooled, the beads were filtered from the aqueous phase, washed with distilled water, then with methanol, and air-dried overnight.

Swelling Measurements

Tea-Bag Method

One gram of polymer sample was placed in a pre-weighed polyester gauze bag and immersed into toluene. The equilibrium swelling was determined by allowing absorption for an overnight. The bag containing swollen sample was hanged for 20 s to remove the excess (interstitial) solvent, and then reweighed. The swelling capacity was calculated as gram of solvent uptake to gram of dry sample.

RESULTS AND DISCUSSION

Bulk and Solution Polymerization

The experimental results of the bulk and solution synthetic methods to produce absorbing polymers are given in Table 1. In bulk polymerization, at a constant concentrations of the monomer, crosslinker (EGDM) and initiator (AIBN), the effect of bath temperature and post-heating of the bulk product was studied.

Generally no viscosity increase was observed upon heating the reaction mixture. This retardation period may be attributed to the presence of

TABLE 1 Bulk and solution polymerization conditions (B- and S-series, respectively), reaction yield and toluene absorbency of the products. Crosslinker (EGDM) 2 Wt.%. EGDM/styrene weight ratio of 0.02 (B-series) and 0.04 (S-series)

Exp.	*Pure initiator, Wt.%*	*Bath temperature, °C*	*Total reaction time, min.*	*Yield, %*	*Absorbency, g/g*
B12	AIBN(0.3)	90	20	66	20.9
B13	AIBN(0.3)	100	17	71	11.0
B15[a]	AIBN(0.3)	90	20	68	9.0
B16[b]	AIBN(0.3)	110	15	70	6.8
B17[c]	AIBN(0.3)	90	1080	77	–
B10	BPO(0.3)	90	50	65	22.3
B8	BPO(1.0)	80	30	60	8.0
S19[d]	BPO(0.9)	Reflux	100	85	10.3
S20[e]	BPO(0.9)	Reflux	93	88	12.7
S21[f]	BPO(0.9)	Reflux	115	79	7.5

[a] As-synthesized gel was heated at 90°C for 1 hr.
[b] As-synthesized gel was heated at 90°C for 3 hr.
[c] As-synthesized gel was heated at 70°C for 18 hr. Reported yield is related to non-purified solid lump product that was too tough to be cut into pieces for absorbency measurements.
[d] Monomer concentration 50 Wt.%. BPO/styrene weight ratio of 0.02.
[e] Monomer concentration 75 Wt.%. BPO/styrene weight ratio of 0.02.
[f] Monomer concentration 30 Wt.%. BPO/styrene weight ratio of 0.02.

oxygen that acts as a free radical scavenger. Since, for practical reasons, the reaction mixture was open to the air, an unrestricted access to oxygen has been provided. The most probable reaction of oxygen, as shown by Barnes [11] and Bamford [12], may be the formation of a copolymer with the monomer (M), i.e., a polyperoxide (Eqs. (1), (2)). This reaction may compete with the addition of normal polymer radical (RM) to the monomer (Eq. (3)). Since addition of monomer to the peroxy radical (Eq. (2)) is much slower than to the normal polymer radical (Eq. (3)), an inhibition or retardation period is often observed. This period (gelation time) often leads to a jelly-like material followed by a real crosslinked gel in case of our experiments.

$$\mathrm{RM}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{R} - \mathrm{O} - \mathrm{O}^{\cdot} \tag{1}$$

$$\mathrm{R} - \mathrm{O} - \mathrm{O}^{\cdot} + \mathrm{M} \rightarrow \mathrm{R} - \mathrm{O} - \mathrm{O} - \mathrm{M}^{\cdot} \tag{2}$$

$$\mathrm{RM}^{\cdot} + \mathrm{M} \rightarrow \mathrm{RM} - \mathrm{M}^{\cdot} \tag{3}$$

Higher reaction rate and yield was achieved at higher bath temperature according to B13 and B16 comparison. The latter sample had less toluene absorption, since heating of the corresponding as-synthesized gel caused continuation of the thermal crosslinking polymerization. The process leads to a higher crosslink density that, in turn, results in a lower swelling and absorbency [13]. Similar conclusion may be made in comparing B12 and B15 experiments. On the other hand, comparing experiments B12 and B13 shows that bath temperatures higher than 90°C resulted in a significant decrease in absorbency for the same reason mentioned above, at the expense of a little decrease of reaction yield and rate. The rate increase is in agreement with the following known Arrhenius-type relationship (Eq. (4)) [14]:

$$\mathrm{LnR_p = LnC + Ln\{[M](f[I])^{1/2}\} - E_R/RT} \tag{4}$$

where R_p and E_R stand for polymerization rate and overall activation energy, and C is constant composed of collision frequency factors of initiation, propagation and termination. [M], [I], R and T are the monomer and initiator concentration, universal gas constant and absolute temperature, respectively.

This equation can also readily be used for explaining why the reaction rate and yield are influenced by either bath temperature or initiator concentration in case of B10 and B8 Exps. With Exp. B17, a long post-heating period led to a very rigid solid product that was too tough for cutting into pieces suitable for absorbency measurements.

In case of solution reactions, although the same crosslinker, EGDM, was used in the solution polymerization of styrene by a couple of researchers [15–17], no clear amounts of the reactants were reported. In the present work, solution polymerization was carried out under reflux (110°C) using a BPO/styrene weight ratio of 0.04 (Tab. 1, S-series). Higher monomer concentration resulted in a higher reaction rate and yield. This observation is also in good agreement with the Eq. (4). Regarding absorbency values, these amounts more or less are affected by all factors influencing the polymer molecular weight. According to the following equation [14], we expect increased number average degree of polymerization (X_n) with increased [M] and T and decreased [I] (C' is a C-type constant and E_{xn} is overall activation energy for the degree of polymerization).

$$\mathrm{LnX_n = LnC' + Ln\{[M]/(f[I])^{1/2}\} - E_{xn}/RT} \tag{5}$$

The relationship can indirectly describe the experimental absorption (swelling) capacity values given in Table 1. Swelling may be assumed as dissolving limited by crosslinks such that the lightly-crosslinked network (gel) will theoretically dissolve at infinite dilution. Meanwhile, increase in molecular weight (here, X_n), which itself was affected by the above-mentioned known parameters, results in a viscosity increase, according to Mark-Hawink-Sakurada $[\eta]$-M_v relationship. If so, higher viscosity in a non-crosslinked polymer means higher swelling for the crosslinked material. Thus, higher monomer concentration in Exp. S20, or lower initiator concentration and higher bath temperature with Exp. B10 (compared to B8) led to higher molecular weight and hence higher toluene absorption.

Suspension Polymerization

In spite of good toluene absorption for some of the experiments listed in Table 1 (i.e., B10 and B12), the bulk and solution methods posses a couple of practical disadvantages mentioned in the experimental section. Therefore, suspension polymerization was chosen as an alternative method. Many attempts were made to achieve higher absorbency, higher yield as well as non-sticky beads, through a practical work-up procedure. The results are summarized in Table 2. Again, in these air-exposed reaction mixtures, a

TABLE 2 Suspension polymerization conditions, yield and toluene-absorbency of products[a]

Exp.	*Suspending agent (SA)*	*SA concentration, Wt.%*	*Yield, %*	*Absorbency, g/g*	*Remarks*
D22	PVA	0.3	91	5.5	Gc[b], D1.7
D24	PVA	0.7	95	6.1	Gc, d2.0
D25	PVA	1.0	94	6.2	Gc, d2.0
D26	PVA	1.5	85	6.0	Gc, d1.5
D30	PVA[c]	0.7	92	6.1	Brittle Gc, d1.0
D27	PVA/PSA[d] (1:1)	0.3	75	6.2	Gc, d1.9
D28	PVA/PSA (1:0.5)	0.3	93	5.4	Gc, d2.2
D29	PVA/PSA (1:2)	0.3	92	5.6	Gc, d2.1
D33[e]	PVA/PSA (1:1)	0.3	58	5.6	Soft adhered beads
D31[f]	SLS/PSA/Na_2SO_4	1.0	66	10.2	Less-diffused beads
D32[g]	As above + Gelatin	1.0	55	11.6	Sticky beads
D34	PVA/SLS (20:1)	0.3	91	6.4	Soft adhered beads
D35[e]	As above	0.3	–	–	Hard lump
D36[h]	As above	0.3	66	8.8	Gc, d7.7
D38[i]	PVA	1.0	90	6.8	Gc, d1.8

[a] All the reactions were carried out at 80°C, stirring rate 400 rpm. Poly(vinyl alcohol) PVA, hydrolysis degree of 98%, Mw 11000–31000. EGDM crosslinker 5 Wt.% of the styrene monomer; pure BPO, 0.5 Wt.% of the styrene monomer.

[b] Grape cluster-like beads of average diameter of d mm as observed by optical microscopy.

[c] PVA with hydrolysis degree of 88%, Mw of 13000–23000.

[d] PSA; Poly(sodium acrylate) as dispersing agent.

[e] EGDM/styrene, 1 Wt.%.

[f] SLS, Sodium laurylsulfate. SLS/PSA/Na_2SO_4 (1:15:50).

[g] Gelatin as the same amount of PSA in aqueous phase.

[h] EGDM/styrene, 2 Wt.%.

[i] A 4-blade baffle (blade width of 8 mm) was used in the reactor.

3 – 4 hr retardation period was observed, for the same reason mentioned in the case of bulk and solution experiments.

Poly(vinyl alcohol), PVA, as a main suspending agent was used in the polymerizations with or without other suspension stabilizers including poly(sodium acrylate), PSA, sodium lauryl sulfate and gelatin. The crosslinker (ethyleneglycol dimethacrylate, EGDM), and initiator (benzoyl-peroxide, BPO), were used at 5 Wt.% and 0.5 Wt.% of the styrene, respectively (except for experiments D33, D35 and D36). With these PVA-stabilized systems, the particles aggregated and diffused into each other, so that each bead looked like a grape cluster (Fig. 1). As observed by a light microscope, individual bead diameter was 1 – 2 mm in average. These cluster particles were easily washed and dried at room temperature and also simply handled. Compared to bulk and solution methods, another advantage of the suspension method was its very higher yield (greater than 90%). Under the constant reactant compositions (Tab. 2), the toluene absorption of the samples was measured as 6 – 11 g/g, which is lower than that of the bulk or solution samples (Tab. 1). This was attributed to the higher amount of EGDM crosslinker in the suspension experiments [13]. With the crosslinker values lower than 2 Wt.% of the styrene monomer, the resultant beads were soft and adhered to each other, besides, very low yield was obtained (Tab. 2, D33, D35 and D36). With two PVA-free formulations [18] (D31 and D32), absorption values were the two highest, at the expense of

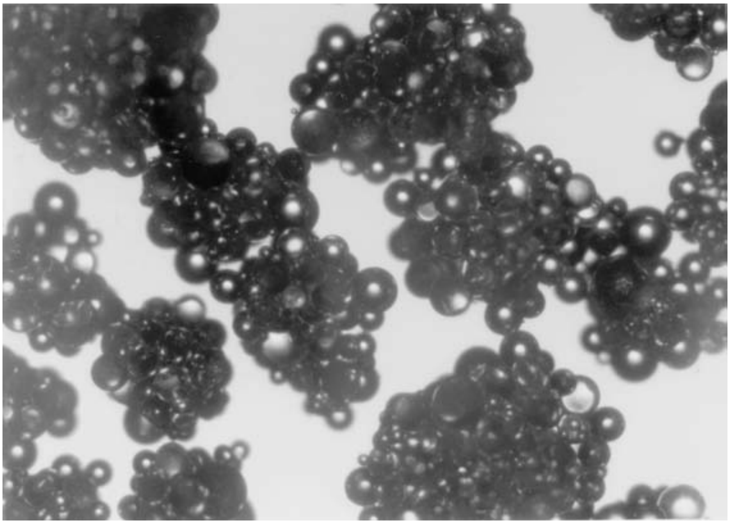

FIGURE 1 A representative photograph of the magnified (× 3.2) particles obtained in suspension polymerization (Exp. D27).

their lower yields. On the other hand, variations of the suspending agent PVA in D22 – D26 experiments showed no certain influence on the yield, particle appearance and liquid absorption. Poly(sodium acrylate), a known dispersing agent [19], showed no appreciable effect on the parameters (D27 – D29). Brittle beads involving smaller particles were obtained by using PVA having a lower degree of hydrolysis (Exp. D30). Finally, increased turbulence of the stirred reaction mixture by placing a four-blades baffle [20] led to no special advantage (D38).

CONCLUSION

To practically prepare absorptive materials being able to uptake and to retain liquid aromatic hydrocarbons, three series of chain AIBN- and BPO-initiated polymerizations were carried out under atmospheric conditions in the presence of ethylene-glycol dimethacrylate (EGDM) as a crosslinker. Although the two highest absorption values were obtained for samples of bulk polymerization (Tab. 1, B10, B12), bulk and solution techniques were not recognized as suitable production methods due to their low yield and a couple of practical disadvantages (see Experimental). Grape cluster-like beads of 1 – 2 mm in size were obtained through PVA-stabilized suspension polymerization at high yield without practical difficulties. The particles showed medium toluene absorption. All the toluene-swollen materials showed good gel strength and holding power.

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