

Some Physicochemical Properties of Methyl Methacrylate-Grafted Nylon 6. II.

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Synopsis

Graft copolymerization of methyl methacrylate on nylon 6 was investigated using KMnO_4 as initiator at 60°C . The optimum conditions of the grafting process using various amounts of methyl methacrylate have been utilized. Physical and chemical properties of the grafted nylon such as moisture regain, density, and infrared spectra are studied. Furthermore, the dyeing behavior of the grafted nylon toward acid and direct dyes is also investigated. The rate of graft copolymerization (R_p) of methyl methacrylate with this system was evaluated and expressed by the following equation depending upon the potassium permanganate concentration used:

$$R_p = K[\text{MMA}]^{1.5} [\text{KMnO}_4]^1 \text{ at } [\text{KMnO}_4] \text{ of } 25 \text{ meq/l.}$$

The degree of polymerization of isolated poly(methyl methacrylate) from the grafted nylon was found to be a first-order dependence.

INTRODUCTION

Recently, most of the advances in research made in textile fibers have been aimed at giving fibers some desirable properties, and a lot of it has been done via graft copolymerization of vinyl monomers onto nylon.¹⁻¹⁰ In a previous article, the optimum conditions for grafting methyl methacrylate onto nylon 6 using KMnO_4 have been reported.¹¹

In this paper, we have further studied detailed kinetic investigations on the graft copolymerization of methyl methacrylate onto nylon 6 initiated by KMnO_4 . Another aspect of this study is to investigate some physical properties of methyl methacrylate-grafted nylon, and the results are discussed in relation to possible structural changes which occurred owing to graft copolymerization.

EXPERIMENTAL

Grafting Procedure

The parent nylon 6 and the grafted fibers are the same as reported in the previous article.¹¹ The monomer and the solvent were used after usual purification. Graft copolymerization was carried out for various reaction times using optimum conditions of initiator (KMnO_4), sulfuric acid, methanol, and

methyl methacrylate concentrations. Details of these conditions are as follows: 25 meq/l. potassium permanganate, 0.4*N* sulfuric acid, 15% methanol, and various concentrations of methyl methacrylate for different reaction times at 60°C at a liquor ratio of 1:100 unless otherwise stated.

The nylon was then extracted with benzene in a Soxhlet apparatus for 16 hr to remove any adhering monomer or homopolymer and was then dried to constant weight was attained. The residual polymer was regarded as the grafted one.

Density and Moisture Regain

The density of the parent and grafted samples was determined by the density gradient column as given by Preston and Minkar.¹² The moisture regain of all the grafted and parent nylon was determined by vacuum desiccator as described by Urqurt and Williams.¹³ Phosphorous pentoxide was used as dehydrating agent.

Infrared Analysis

The infrared spectra of the parent nylon and grafted samples were recorded on a fully automatic UR10 spectrophotometer using a KBr pellet technique as described by Nasser and Moharram.¹⁴

Dye Uptake

Dyeing of parent nylon and nylon grafted with 10–75% poly(methyl methacrylate) was carried out using two different dyes under the following conditions. The material:liquor ratio was 1:500. The dye bath was prepared from 2% dye solution. The dyeing proceeded at 60°, 80°, and 100°C, respectively. Small aliquots at different times up to 1 hr were withdrawn, and the dye uptake was found by using a Carl Zeiss spectrophotometer.

Acid dye (Benzyl Fast Red B CIBA) was used, and the bath contained 2% glacial acetic acid and 10% Glauber's salt. The final pH of the bath was adjusted at 3–4.

Direct cotton dye (Sirius Light Scarlet G-LL (Bayer) was used. The bath contained 2% glacial acetic acid and 10% Glauber's salt.

Separation of Grafted Polymer from Nylon

Poly(methyl methacrylate) grafted onto nylon was isolated by hydrolysis of 0.2 g grafted nylon with 20 ml concentrated HCl and 20 ml of 90% glacial acetic acid at 100°C for 2 hr as described by Arai and Negishi.¹⁵

Determination of Molecular Weight

The number-average molecular weight (\bar{M}_n) of the isolated poly(methyl methacrylate) from the grafted nylon was measured in an Ubbelohde viscometer in benzene as described by Fox et al.¹⁶ according to the following equation:

$$[\eta] = 8.9 \times 10^{-5}(\bar{M}_n)^{0.75}$$

where $[\eta]$ is the intrinsic viscosity of the polymer in g/dl.

RESULTS AND DISCUSSION

Graft copolymerization of methyl methacrylate onto nylon 6 was performed in the presence of potassium permanganate, sulfuric acid, and methanol as well as methyl methacrylate at 60°C. Since the grafting of methyl methacrylate proceeds by this system at a moderate rate, the behavior of this polymerization was investigated kinetically and the rate equations were determined.

Dependence of R_p on Monomer Concentration

The log-log plots of the rate of graft polymerization (R_p) and the methyl methacrylate concentration are shown in Fig. 1. Here, the concentration of potassium permanganate was kept constant at 25 meq/l. at 60°C. As can be seen, the rate of grafting R_p increases with increasing monomer concentration. This means that the monomer participates in the grafting process. Such a trend has also been noted in other systems.¹⁷⁻¹⁹

Dependence of R_p on Potassium Permanganate Concentration

Figure 2 illustrates the relation between the rate of grafting R_p and the concentration of potassium permanganate in a log-log plot. Here, the

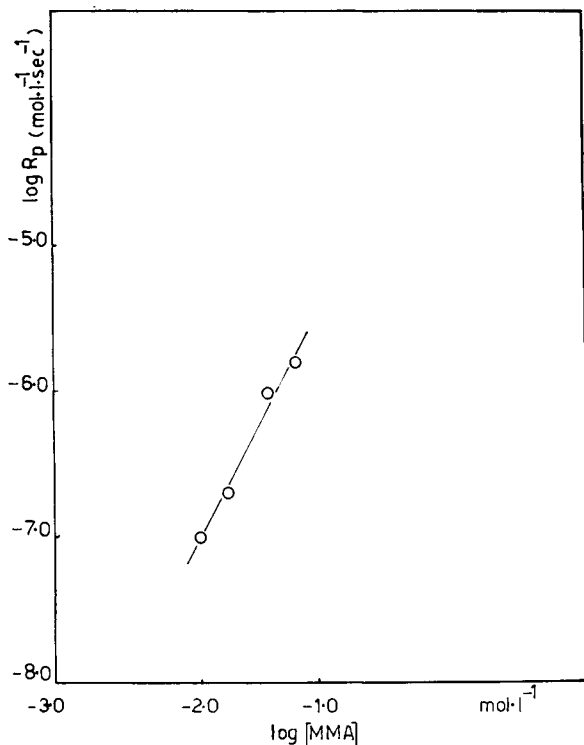


Fig. 1. Relation between rate of polymerization R_p and methyl methacrylate concentration [MMA] at 60°C: 25 meq/l. KMnO_4 , 15% methanol, 10 ml 2N H_2SO_4 , reaction time 30 min, and liquor ratio 1:100.

amounts of methyl methacrylate, methanol, nylon, and sulfuric acid were kept constant. The concentration of potassium permanganate was varied within the range of 5 to 25 meq/l. The rate of grafting R_p was found to increase with increase in potassium permanganate concentration.

From all these, the following rate equation can be drawn for the graft copolymerization of methyl methacrylate with this initiator system:

$$R_p = K[\text{MMA}]^{1.5} [\text{KMnO}_4]^1 \text{ at } [\text{KMnO}_4] \text{ of } 25 \text{ meq/l.}$$

The above equations are very complicated as compared with those reported for radical polymerization with typical initiators such as peroxide or azobisisobutyronitrile. It must be considered that these compounds of the initiator system do participate in the process, especially in initiation and termination in a complicated manner. The observed high-order (1.5) dependence of R_p on the methyl methacrylate concentration (Fig. 1) seems to be associated with pronounced acceleration of methanol as a solvent.

Kinetic studies for uncatalyzed graft copolymerization reported by Imoto et al.¹⁷ showed that the rate of polymerization R_p was proportional to the amount of macromolecules when the amount of methyl methacrylate is small and the degree of polymerization is high according to the following equation:

$$R_p = K[\text{Nylon}]^1 [\text{MMA}]^{1.0 \rightarrow 0.0}$$

It is clear that the results obtained from the potassium permanganate-methyl methacrylate-nylon system are similar to those reported by Narita et

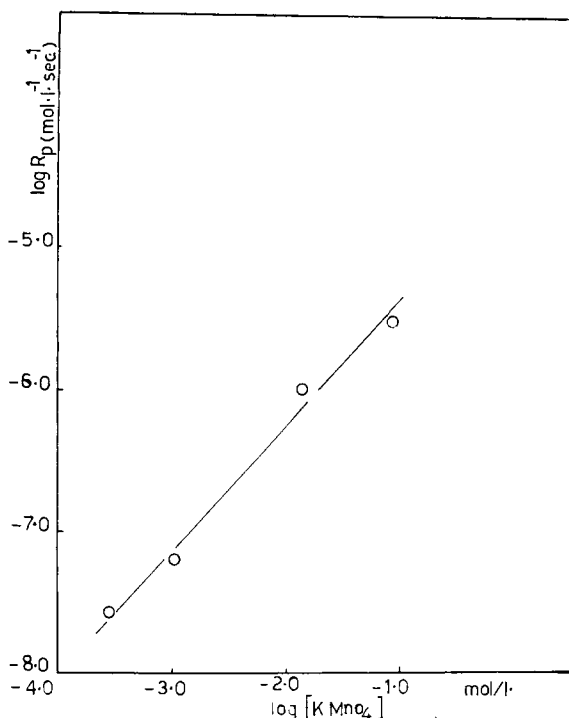


Fig. 2. Relation between rate of polymerization R_p and potassium permanganate concentration at 60°C: 4% methyl methacrylate, 15% methanol, 10 ml 2N H₂SO₄, reaction time 30 min, and liquor ratio 1:100.

al.¹⁸ for the polymerization of methyl methacrylate initiated with ferric nitrate. This is also confirmed by Geczy and Abdel-Fattah¹⁹ for the graft copolymerization of methyl methacrylate onto wool induced by the hydrogen peroxide–thiosulfate redox system.

The results obtained in this investigation indicate that the rate of graft polymerization R_p is dependent upon the amount of potassium permanganate concentration up to 25 meq/l. This is also supported by the work of Misra and Gupta²⁰ for the aqueous polymerization of methyl methacrylate initiated by potassium permanganate–oxalic acid redox system. These authors showed also that the catalyst exponent of potassium permanganate decreases from nearly unity to 0.66 with increase in concentration of the catalyst. This was attributed to participation of primary radicals in the termination of the growing chain.

Number-Average Molecular Weight

The number-average molecular weight \bar{M}_n of the separated methyl methacrylate from grafted nylon in the presence of constant methanol concentration (5 moles/l.) was estimated, using benzene as a solvent. Figure 3. shows the relation between the degree of polymerization and methyl methacrylate concentration. This shows that the degree of polymerization of methyl methacrylate is proportional to the monomer concentration and is of first-

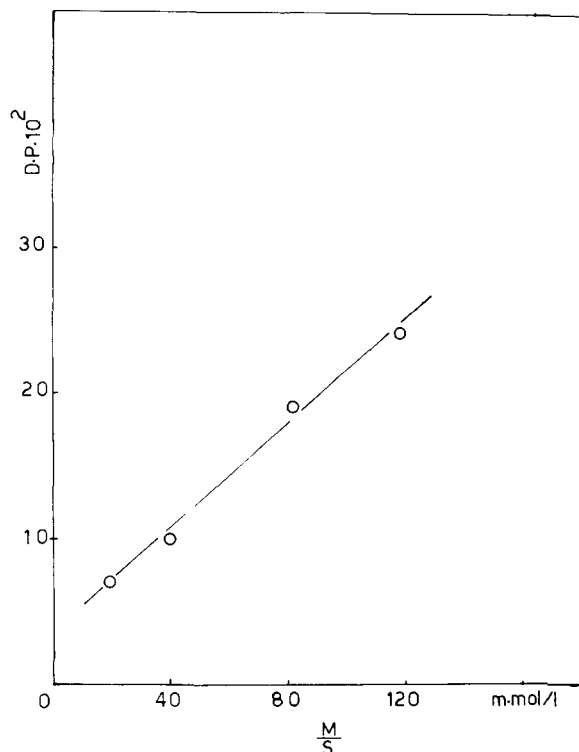


Fig. 3. Relation between degree of polymerization (D.P.) and methyl methacrylate concentration $[M/S]$, where $[M]$ is the monomer and $[S]$ is the solvent concentrations in mmoles/l.

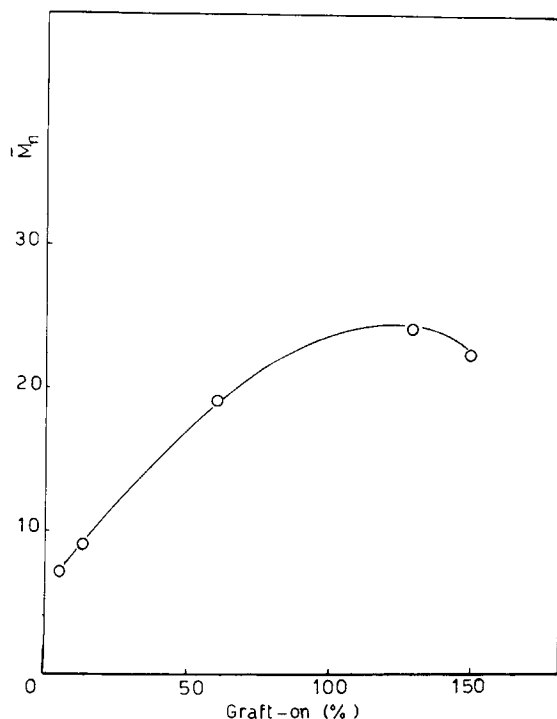


Fig. 4. Relation between number-average molecular weight \bar{M}_n of grafted poly(methyl methacrylate) onto nylon and graft-on %.

order dependence. It is seen also that the monomer participates in the initiation step while termination takes place between two growing radicals. This is in agreement with the statements of Geczy and Abdel-Fattah¹⁹ for the graft copolymerization of methyl methacrylate onto wool.

Figure 4 shows the number-average molecular weight \bar{M}_n of isolated poly(methyl methacrylate) from grafted nylon versus grafting percentage. It can be noted that the number-average molecular weight increases with increase of add-on percentage, but exhibits a maximum value which tends to shift in position to the side of greater graft-on with increasing monomer concentration. Although this behavior is complicated, it should be considered on the basis of diffusion of monomer within the sample. This result was also reported by Negishi et al.²¹

Infrared Analysis of Methyl Methacrylate-Grafted Nylon

Figure 5 illustrates the infrared spectrum of parent and grafted nylon with different graft yield percentages. It can be seen that the only difference between the spectra of methyl methacrylate-grafted samples with 15.4% graft-on and those of the parent sample is the increase in intensities of the original bands; whereas in the sample grafted with 75.2% there are noticeable variations in the absorption bands as follows:

a. The appearance of a band at 1730 cm^{-1} which corresponds to the absorption of C—O groups. This exhibits the characteristic band of the ester group of poly(methyl methacrylate) as reported by Arai et al.²²

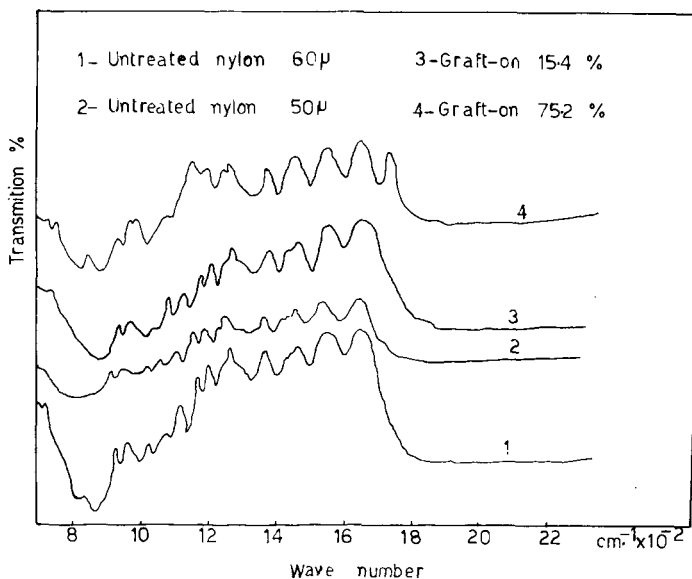


Fig. 5. Infrared spectrum of grafted and ungrafted nylon with different mesh size (0.210–0.124 mm.) for ungrafted nylon.

b. Disappearance of the band at 1030 cm^{-1} which corresponds to —CONH— groups in plane vibration and 1120 cm^{-1} due to C—C stretching. This was revealed also by Sanderman and Keller.²³ Furthermore, the splitting of the 970 cm^{-1} band as —CONH— in plane vibration into doublet at 965 cm^{-1} and 985 cm^{-1} besides the appearance of the band at 835 cm^{-1} which corresponds to the absorption of $\text{—CH}_2\text{—}$ group rocking.

c. The increase in intensities of the original bands of nylon 6. From the

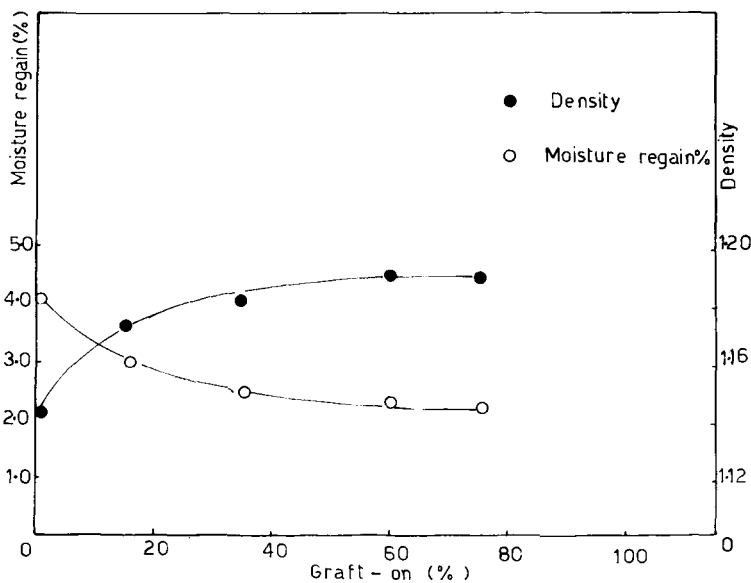


Fig. 6. Effect of grafting on density and moisture regain percentages.

view of the structure of nylon 6 grafted with methyl methacrylate, it is noted that the amorphous content increases, which means a decrease in the degree of crystallinity.

Moisture Regain and Density of Grafted Nylon

The treatment of nylon 6 with methyl methacrylate-potassium permanganate system results in a decrease in the moisture regain as well as an increase in the density of the grafted samples compared to the parent nylon (Fig. 6). This could be ascribed to the deposition of the poly(methyl methacrylate) in the amorphous regions of the samples and to the hydrophobic nature of this polymer.²⁴

Dye Uptake

A series of nylon samples with 10-75% add-on of poly(methyl methacrylate) was prepared by varying the concentrations of the monomer and initiator. Dyeing of control sample and methyl methacrylate-grafted sample was carried out at 60°, 80°, and 100°C, respectively, using acid dye (Benzyl Fast Red B) and direct dye (Sirius Light Scarlet G-11). The results for the dye uptake and the graft yield percentage are illustrated in Tables I and II and represented by Figures 7 and 8, respectively.

It can be seen that the initial rate of dye uptake on grafted nylon was slower than with the control sample. It seems also that the dye uptake on grafted samples with acid and direct dye increases slightly with increase in tempera-

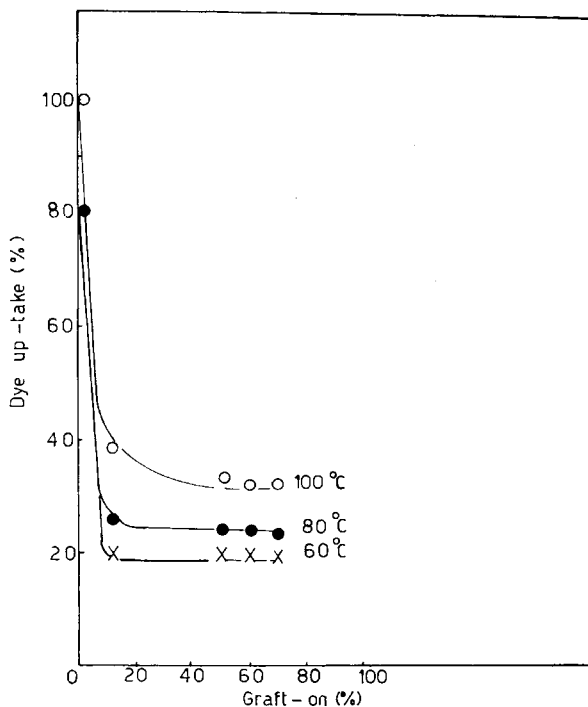


Fig. 7. Dyeability of methyl methacrylate-grafted nylon fibers at various temperatures using dye (Benzyl Fast Red B).

TABLE I
Acid Dye (Benzyl Fast Red B) Uptake on Grafted Nylon

Graft yield, %	Dyeing temp., °C	Dye uptake, %					
		10 min	20 min	30 min	40 min	50 min	60 min
10.0	60	8	10	10	10	10	10
	80	10	10	10	10	10	10
	100	12	12	13	13	13	13
15.4	60	7	8	8	8	8	8
	80	10	10	10	10	10	10
	100	10	12	13	13	13	13
46.4	60	6	8	8	8	8	8
	80	10	10	10	10	10	10
	100	10	12	12	12	12	12
75.2	60	6	8	8	8	8	8
	80	6	10	10	10	10	10
	100	10	12	12	12	12	12

ture up to 100°C. However, with increase in grafting percentage, the dye uptake on the grafted samples decreases gradually. On the other hand, differences in the graft yield percentages on nylon from 10 to 75 do not affect the dye uptake. This may be due to deposition of poly(methyl methacrylate) in the pores of nylon fibers and to the physical entanglement of the grafts at higher graft-on percentage, preventing the dye molecules from penetrating into the amorphous portions. Varma et al.²⁴ have noted also that nylon

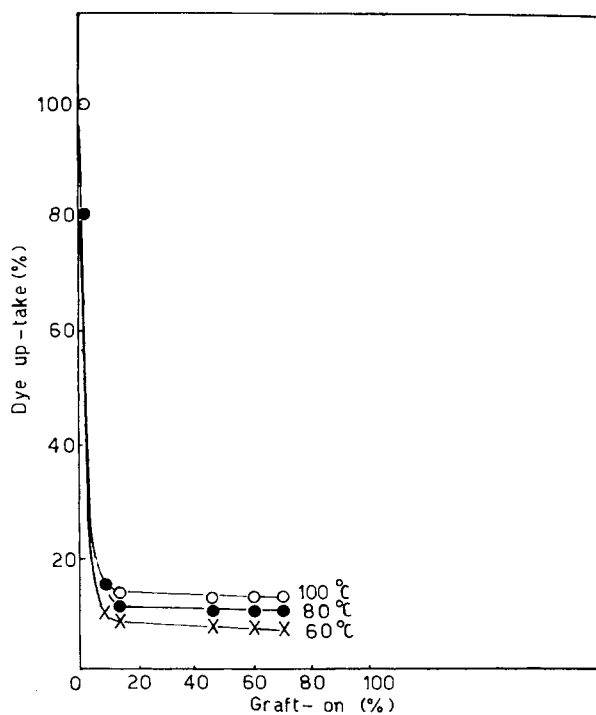


Fig. 8. Dyeability of methyl methacrylate-grafted nylon fibers at various temperatures using direct dye (Sirius Light Scarlet G-11).

TABLE II
Direct Dye (Sirius Light Scarlet G-11) Uptake of Grafted Nylon

Graft yield, %	Dyeing temp., °C	Dye uptake, %					
		10 min	20 min	30 min	40 min	50 min	60 min
10.0	60	13	17	17	17	18	18
	80	20	24	25	25	25	25
	100	30	33	35	37	37	38
15.4	60	13	15	17	18	18	18
	80	18	23	25	25	25	25
	100	30	35	35	36	36	36
46.4	60	13	15	17	17	17	17
	80	18	23	25	25	25	25
	100	26	30	32	32	34	34
75.2	60	10	13	15	16	16	16
	80	18	21	22	23	23	23
	100	26	30	30	30	30	30

grafted with methyl methacrylate or methacrylic acid has less affinity for disperse dye than the untreated nylon. It must be mentioned also that the decrease in dye uptake of grafted nylon may be accounted for from the decrease in moisture regain and to the hydrophobic nature of poly(methyl methacrylate).

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