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SWELLING PROPERTIES OF METHYL METHACRYLATE COPOLYMERS PREPARED BY GAMMA IRRADIATION

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ABSTRACT

Bulk polymerization and copolymerization have been affected to >95 conversion by λ-irradiation. Polymers of methyl methacrylate (MMA) and its copolymers were prepared with 2-hydroxyethyl methacrylate (HEMA), hexamethyl disiloxane (HMDS), and polypropylene glycol (PPG) in the presence and absence of a crosslinking agent. The optical homogeneity (classified as opacity, transluceny or transparency), density, equilibrium water content, percent hydration, and thermal properties were examined. The influences of dose, presence of crosslinker amount and type of comonomer on these properties were investigated.

INTRODUCTION

Polymethyl methacrylate and copolymers of methyl methacrylate accupy a singificant role as a biomedical material. Optical characteristics of polymetyl methacrylate, its resistance to discoloration, its light weight and excellent molding and machining qualities, as well as the lack of irritation or allergic response in patients have been important factors (Refojo, 1979). The preparative techniques usually involve polymerization of methyl methacrylate or copolymerization of a hydrophobic methyl methacrylate and alkyl acrylates with a hydrophilic monomer in the presence and absence of a crosslinking agent and bulk polymerization or copolymerization in vacuo initiated by γ-irradiation is often used (Singh et al. 1980, Huglin and Zakaria, 1983).

A xerogel is a crosslinked polymer or copolymer, which is capable of imbibing a considerable quantity of liquid up to swelling equilibrium. With water as swelling agent, the product is termed a hydrogel (Wichterle, 1971, Ratner and Hoffman, 1976). The final water content is dependent on the chemical composition and also, in the majority of cases, on the crosslinking density. A straight forward means of effecting a range of water contents is by copolymerizing a hydrophobic monomer with a hydrophilic one. Much of the extensive literature on the preparation and properties of hydrogels in concerned with biomedical applications (Pedley et al, 1980). In addition the requirement of appreciable water content (vehicle for oxygen transport), some particular application demands high light transmission. Accordingly, attention has been focused on the conditions necessary to obtain materials which are optically clear not only as xerogels but also in the state of ultimate use, i.e hydrogels.

EXTERIMENTAL

Materials: MMA was supplied by Fluka A.G. and was used after the removal of the inhibitor by NaOH extraction followed by vacuum distillation. PPG (MW: 1025) and n-octane were supplied by BDH and were used as received. HMDS was supplied by Fluka A.G., and used as received. Ethylene glycol dimethacrylate (EGDMA) and HEMA were supplied by Poly Sciences Inc., purified by vacuum distillation.

Methods: Required amount of chemicals were placed in glass tubes, flushed with nitrogen gas and then the tubes were flame sealed under nitrogen atmosphere or under vacuum. The solutions were completely mixed using a vortex, subjected to ^{60}Co gamma irradiation and cured at 100°C for 1.5 h. The polymeric rods were then weighed, washed several times with distilled water, dried in a vacuum oven and then reweighed. Percent polymerization was determined from the weight differences.

IR spectra were taken by using Perkin-Elmer 1430 IR Spectrophotometer.

Percent equilibrium water content (% EWC) and percent hydration (% H) values were obtained from the weight differences of dry and swollen samples by using the equations;

$$\% \text{ EWC} = (\text{wet vt-dry wt/wet wt}) (100) \tag{1}$$

$$\% \text{ H} = (\text{wet wt-dry wt/dry wt}) (100) \tag{2}$$

Density of the dry and swollen samples were measured by using a pycnometer and n-decane was chosen as the inert liquid. DSC runs were carried out in Dupont 910 Differential Scanning Calorimeter. TGA were carried out in a Dupont TGA - 951 model 1090 thermal analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The samples were examined visually for homogeneity and transpareney (Table-1). The pure PMMA samples, PMMA1 and PMMA2 were translucent and /or heterogeneous because of the presence of bubbles in them. Addition of a crosslinker, ethylene glycol dimethacrylate, leads clear, transparent and very homogeneous polymers. For these samples, even the applied gamma dose was not high, the polymerization was complete above 95 percent. The reason for this is the thermal continuation of the polymerization during the curing process.

Heterogeneity because of phase separation was observed in the P(MMA-co-HMDS) although the polymerization was found to be completed more than 99 percent.

The P(MMA-co-HEMA) were all clear transperent and homogeneous and for all samples polymerization was 100 percent complete.

Table 1. Properties of the Polymers.

Sample	EGDMA (mmol)	mol [CM]* / mol [MMA]	Reaction* Medium	Dose (KGy)	Visual Apperance	Polymerization (%)
PMMA1			V	32	translucent	97.80
PMMA2			V	1880	translucent	99.96
PMMA3	0.106		N	45	transparent	100.00
PMMA4	1.060		N	45	transparent	100.00
PMMA5	2.120		N	45	transparent	100.00
P(MMA-co-HMDS)1		0.100	V	728	heterogen	99.77
P(MMA-co-HMDS)2		0.100	V	2880	heterogen	99.84
P(MMA-co-HMDS)3	1.106	0.100	N	196	opaque	100.00
P(MMA-co-PPG)1		0.010	V	3232	transparent	99.96
P(MMA-co-PPG)2		0.025	V	3232	opaque	98.47
P(MMA-co-PPG)3		0.050	V	3232	opaque	98.39
P(MMA-co-PPG)4		0.075	V	3232	opaque	93.87
P(MMA-co-PPG)5		0.100	V	3232	opaque	91.46
P(MMA,co-PPG)6	0.106	0.020	N	3232	transparent	100.00
P(MMA-co-PPG)7	0.106	0.040	N	3232	transparent	99.98
P(MMA-co-PPG)8	0.106	0.060	N	3232	opaque	99.96
P(MMA-co-HEMA)1		0.100	V	1688	transparent	100.00
P(MMA-co-HEMA)2		0.100	V	2880	transparent	100.00
P(MMA-co-HEMA)3	0.106	0.100	N	30	transparent	100.00
P(MMA-co-HEMA)4	0.106	0.200	N	30	transparent	100.00
P(MMA-co-HEMA)5	0.106	0.500	N	30	transparent	100.00
P(MMA-co-HEMA)6	0.106	0.750	N	30	transparent	100.00

* CM = Comonomer

** V = Vacuum, N = Nitrogen

For the P(MMA-co-PPG) only the samples P(MMA-co-PPG)1, P(MMA-co-PPG)2, P(MMA-co-PPG)6 were transparent and all the others were homogeneous but opaque. Opacity increased as the PPG content increased. Percent polymerization values for these samples decreased from 99.96 to 91.46 as the mole ratio of PPG to MMA was increased from 0.01 P(MMA-co-PPG)1 to 0.10 P(MMA-co-PPG)5. The reason for this decrease is the nonexistance of unsaturation in PPG structure. On the other hand presence of a crosslinker in the medium causes an increase in the percent polymerization values.

For PMMA, % EWC is given less than 2 % in the literature (Lyndon, 1986) and was found as 2.24 and 2.05 for samples PMMA1 and PMMA2, respectively (Table-2). Addition of hydrophobic HMDS, decreased this value to 1.25 for P(MMA-co-HMDS) sample. Addition of hydrophilic PPG, HEMA into copolymer structure caused an increase in % EWC. Addition of a crosslinker into the medium would cause a decrease in the swelling properties and it was observed for the samples PMMA3, P(MMA-co-HMDS)^3 and P(MMA-co-HEMA)3. It was also found that, there was a decrease in % EWC values as the applied gamma dose was increased.

Table 2. Equilibrium Water Content, Hydration and Density Values.

Sample	EWC (%)	H (%)	Dry Density (gcm^{-3})	Swollen Density (gcm^{-3})
PMMA1	2.24	2.29	1.218	1.147
PMMA2	2.05	2.00	1.185	1.088
PMMA3	1.63	1.65	1.166	1.152
P(MMA-co-HMDS)1	2.95	3.05	1.105	1.105
P(MMA-co-HMDS)2	2.76	2.84	1.115	1.078
P(MMA-co-HMDS)3	1.25	1.27	—	—
P(MMA-co-PPG)1	1.75	1.79	—	—
P(MMA-co-PPG)2	8.61	9.42	0.915	0.932
P(MMA-co-PPG)3	8.885	9.71	0.954	0.965
P(MMA-co-PPG)4	24.77	32.93	0.978	1.039
P(MMA-co-PPG)5	31.09	45.12	1.028	1.072
P(MMA-co-PPG)6	1.83	1.86	—	—
P(MMA-co-PPG)7	1.93	1.96	—	—
P(MMA-co-PPG)8	2.30	2.35	—	—
P(MMA-co-GEMA)1H	3.80	3.95	1.145	1.069
P(MMA-co-HEMA)2	3.58	3.71	1.214	1.157
P(MMA-co-HEMA)3	1.97	2.01	1.010	1.005
P(MMA-co-HEMA)4	3.38	3.50	1.041	1.031
P(MMA-co-HEMA)5	8.12	8.83	1.211	1.104
P(MMA-co-HEMA)6	13.42	15.51	1.156	1.135

The density of PMMA is given as 1.188 (Gall and McCrum, 1961) and it was found as 1.218 for PMMA1 and 1.185 for PMMA2 and 1.166 for PMMA3 samples (Table-2). The use of crosslinker and the prosess of polymerization affect the values obtained. In the case of copolymers, it has been observed that addition of comonomer in the polymerization mixture gives first a decrease down to 0.195 for PPG and 1.010 for HEMA and further addition couses an increase. This can be explained as; addition of small amount of comonomer disturbs the regularity of PMMA chains, prevents their close coming and these decrease the density. But further addition will form a new order between the chains and will cause an increase in the density (Figure 1).

TGA examination of PMMA 1 showed that above 200°C degradation starts and at about 400°C 0.5 % residue remains (Figure 2). DSC examination for the same sample showed an endothermic peak at about 105°C indicating Tg of PMMA and an exothermic peak about 140°C showes some new arrangements. Above 200°C continuous absorption of heat indicates continious degradation of the sample (Figure 3). For P(MMA-co-HMDS)2, weight decrease about 3 % was observed at 140°C from TGA examination and this is also seen in DSC results as an endothermic peak. The reason might be release of HMDS or release of some other compounds formed during polymerization. In the case of P(MMA-co-HEMA)2 an endothermic peak, at 120°C was observed and continuous heat absorption and degradation started above 180°C. For P(MMA-co-PPG)2, an endothermic peak has shifted to 70°C and degradation starts above 230°C.

The IR spectrum of the samples also yield information about copolymer compositions (Figure 3). The carbonyl absorption at 1710 cm^{-1} was chosen as the reference peak height ratios were calculated for some identifiying peaks (Table-3). As a result of these observations, it can be stated that the comonomer added to the starting mixture take part in the network structure.

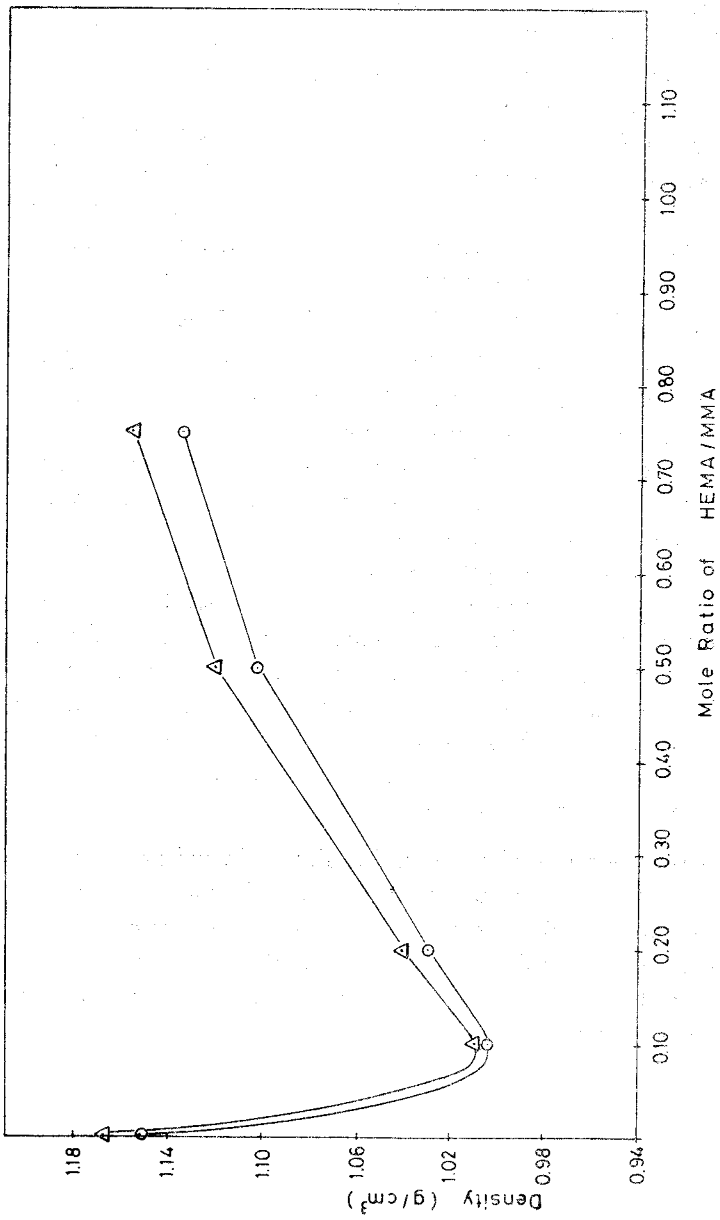

Figure 1. Density vs. Mole Ratio of HEMA/MMA for P(MMA-co-HEMA)
△ : Dry, ⊙ : Swollen.

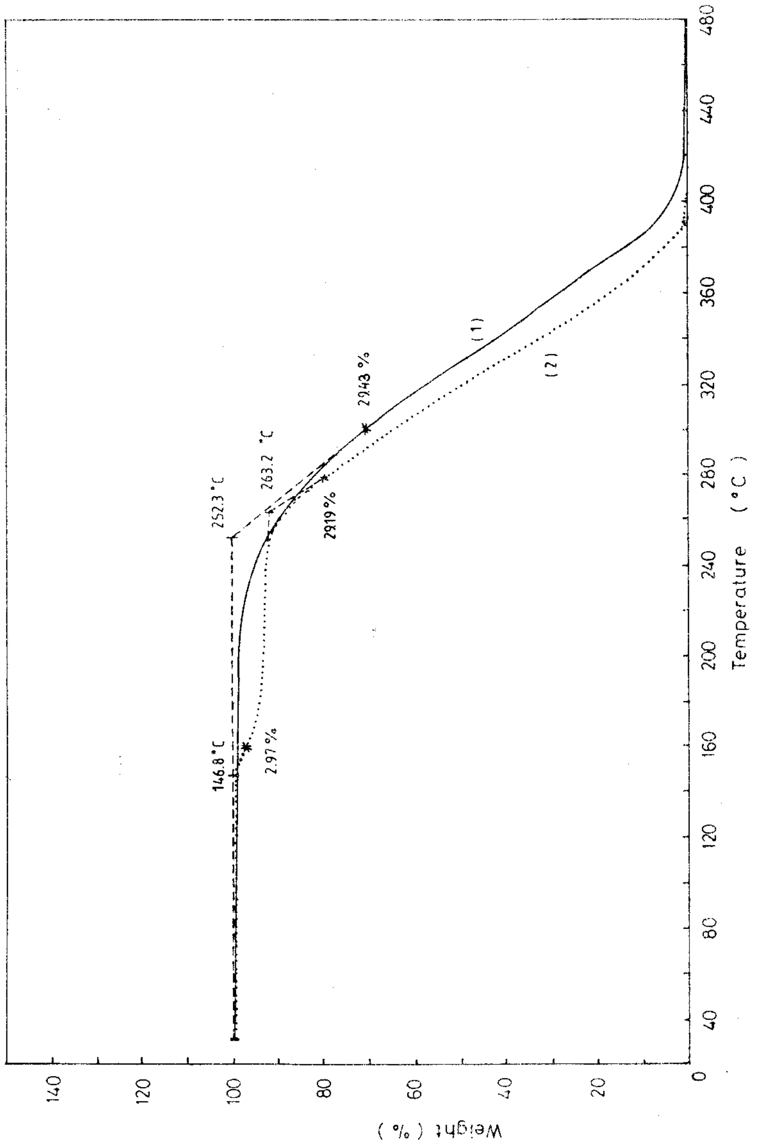

Figure 2. TGA Curves of (1) **PMMA1**, (2) **P(MMA-co-HMDS)2**.

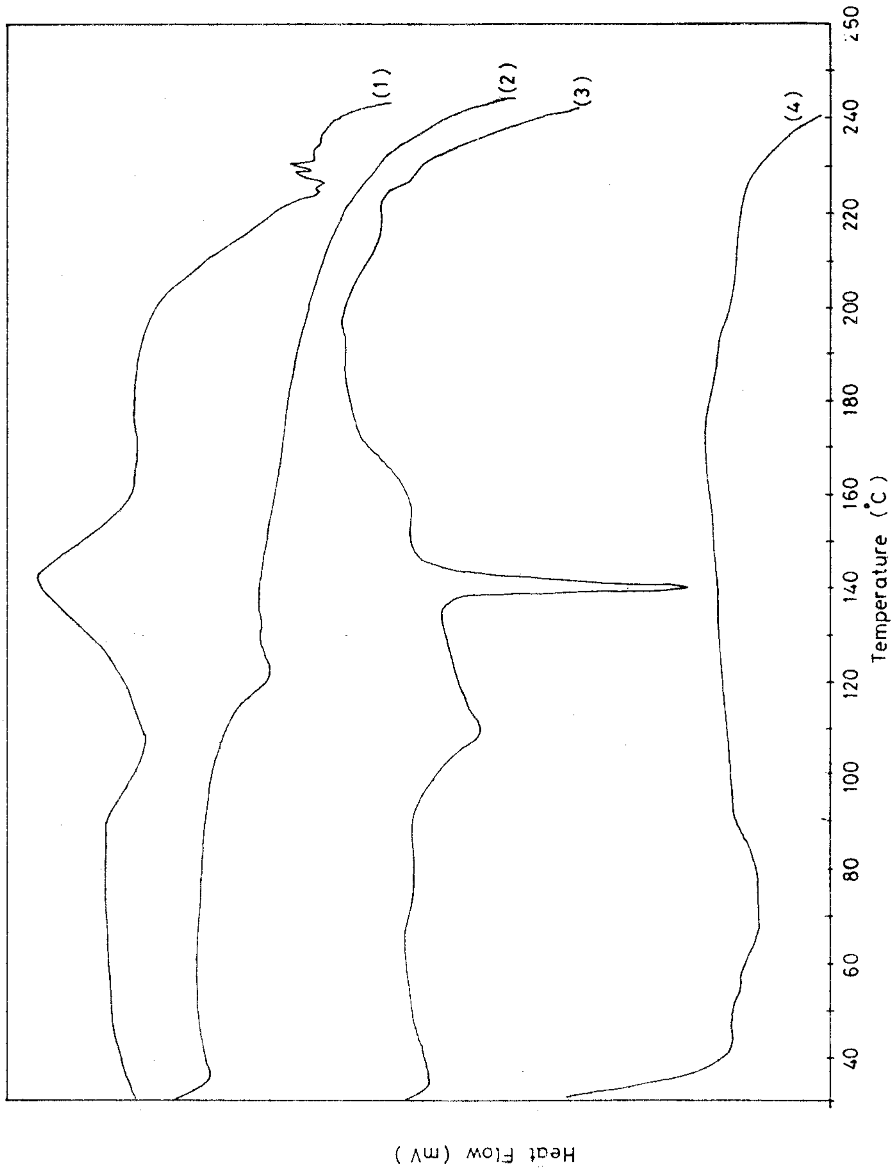

Figure 3. DSC Curves of (1) PMMA1, (2) P(MMA–co–HEMA)2 (3) P(MMA–co–HMDS)2, (4) P(MMA–co–PPG)2.

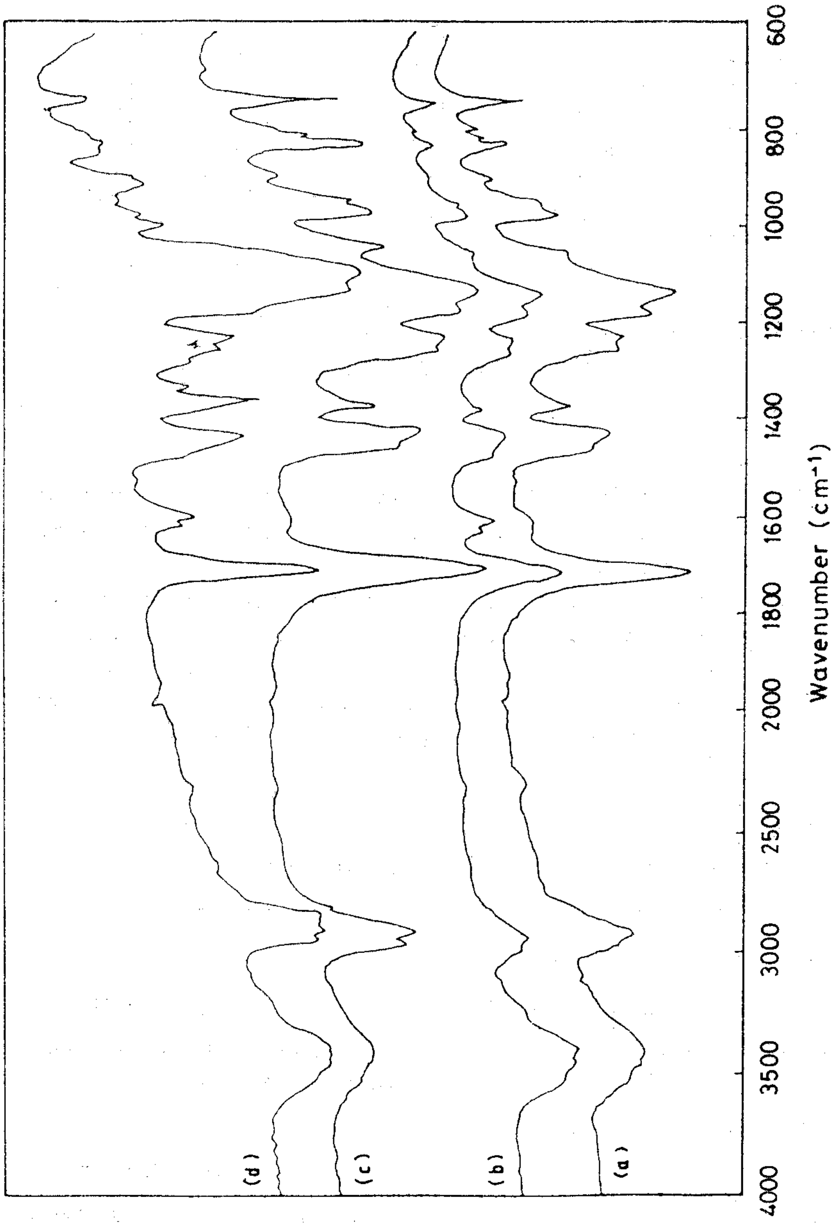

Figure 4. IR Spectrum of (a) PMMA, (b) P(MMA-co-HEMA), (c) P(MMA-co-HMDS), (d) (MMA-co-PPG)

Table 3. Some Characteristic Peak Height Ration of Copolymers.

Sample	Bonds	Absorption Wavenumbers (cm^{-3})	Ratio in PPMA	Ratio in Copolymer
P(MMA-co-HEMA)2	$OH/C=O$	3400/1710	0.318	0.700
	$CH_2/C=O$	2920/1710	0.397	0.425
	$CH_2/C=O$	1450/1710	0.483	0.500
P(MMA-co-HMDS)$_2$	$Si-O-Si/C=O$	1050/1710	0.000	0.282
	$Si(CH_3)_3/C=O$	840/1710	0.000	0.615
	$OH/C=O$	3400/1710	0.318	0.412
	$C-O-C/C=O$	1100/1710	0.000	1.250
(PMMA-co-HEMA)4	$CH_2OH/C=O$	1000/1710	0.000	0.176
	$CH_2OH/C=O$	1290/1710	0.000	0.250
	$C-OH/C=O$	1340/1710	0.000	0.279

ÖZET

Polimetil metakrilat ve metil metakrilatın 2-hidroksietil metakrilat, hegzametil disiloksan, polipropilen glikolle kopolimerleri çapraz bağlayıcı madde kullanılarak veya kullanılmadan γ ışınlarıyla kütle polimerizasyonu ve kopolimerizasyonu sonucunda elde edilmiştir. Kullanılan doz miktarına, çapraz bağlayıcı madde yapısına ve miktarına, komonomer yapısına ve miktarına bağlı olarak hazırlanan polimer ve kopolimerlerin değişik optik homojenlik, yoğunluk, denge su miktarı, yüzde hidrasyon ve termal özellikler gösterdiği görülmüştür.

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