Molecular Weight Distribution of the Graft Copolymer Comprising Mixtures of Styrene and Acrylamiae on Cellulose Acetate Film by means of Gel Permeation Chromatography

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Synopsis

Styrene portion of the radiation-induced graft copolymer comprising styrene and acrylamide was separated by acid hydrolysis and the effects of various grafting parameters (e.g., reaction time, reaction temperature, solvents, monomer composition, etc.) on molecular weight distribution were evaluated by means of gel permeation chromatography. When a single monomer or mixture of two monomers are grafted, the molecular weight is found to increase, but polymer dispersity decreases with the increase of reaction time or reaction temperature except at a higher reaction time due to the continuous enlargement of the growing chain through increased swelling and molecular motion of the trapped radicals. At higher reaction time the degradation of the graft chains lead to lower molecular weight and higher polymer dispersity. Effects of solvents (e.g., methanol, ethanol, and t-butanol) on the molecular weight and molecular weight distribution were discussed on the basis of swelling property and chain transfer constants of the solvents. Styrene-type graft radical being long lived compared to acrylamide type, gave long-chain styrene graft with the increase of styrene content in the reaction mixture. A comparison of the effect of one- and two-component systems on a molecular weight distribution is also discussed.

INTRODUCTION

Properties of a graft copolymer depend on the extent of graft copolymerization as well as on the molecular weight and molecular weight distribution of the grafted chains.[1] Various grafting parameters, such as temperature, reaction time, reaction medium, and so on, play important roles to control the molecular weight as they influence the extent of graft copolymerization. Gel permeation chromatography (GPC) is an excellent fractionation tool to characterize graft copolymers.[2] A detailed investigation of molecular weight with the change of various grafting parameters is scarcely studied.[3-7] A prior separation of the grafted branch is, however, essential for the determination of molecular weight by this method. But the separation of grafted branch is a difficult job, especially when the grafted branch comprises two monomers[8] having different properties. Even after the separation of the two types of branches in this investigation, two different monomers (e.g., styrene and acrylamide), could not be characterized by GPC. On the the styrene branch of the graft copolymer was evaluated by this method. The molecular weight and molecular weight distribution of the isolated graft were then studied. Effects of various parameters (e.g.,

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solvents, solvent composition, reaction time, reaction temperature, monomer composition), on molecular weight and molecular weight distribution were evaluated.

EXPERIMENTAL

Graft copolymerization of styrene and acrylamide onto cellulose acetate were carried out by the preirradiation technique. The detailed procedure for the preparation of graft copolymer has been reported earlier.[9]

Gel permeation chromatograms were recorded in Du Pont HPLC-860 having ultraviolet (UV) detector. The liquid chromatograph consists of columns (6.2 mm ID $\times$ 25 cm) comprising Zorbax PSM 60S and Zorbax PSM 1000S in order that a wide range of molecular weight (10^2–10^6) materials may be studied. Tetrahydrofuran (THF) was used as the eluent and this was purified[10] by refluxing for ~48 h over potassium metal followed by vacuum distillation. Purity of the solvent (THF) was examined by UV spectrophotometer. The GPC columns were calibrated with known standards of polystyrene samples supplied by Du Pont. For each experiment 3 mg/ml of samples was used. The flow rate of the eluent was 1 ml/min. The standard program provided by Du Pont along with the molecular weight distribution-1 data analyzer was also used for data analysis for determining the distribution of molecular weights.

The grafted side chains were isolated from the cellulose acetate backbone by subjecting to acid hydrolysis.[7,11] About 0.5 g grafted copolymers were swollen at room temperature in 15 ml dioxane for a period of ~20 h and then 3 ml 6N HCl was added slowly and the whole was refluxed in a water bath for 2-2$\frac{1}{2}$ h. The contents were cooled and poured into 50 cc ice-cold methanol with vigorous stirring when polystyrene was precipitated out. The collected precipitate was washed with methanol and dissolved in benzene and reprecipitated by methanol. This process was repeated twice. The infrared (IR) analysis of the grafted polystyrene branch showed no contamination due to polyacrylamide-grafted branch and cellulose acetate.

RESULTS AND DISCUSSION

The effects of various grafting parameters (e.g., temperature, reaction time, composition of solvents, and composition of monomers on the molecular weight) as well as on its distribution are shown in Tables I and II.

During grafting a single monomer (styrene), when the temperature of the grafting reaction is increased keeping the other grafting conditions fixed, the molecular weight as well as the dispersity factor ($\overline{M}w/\overline{M}n$) gradually increase (Table I). With the increase of reaction temperature, the increased swelling and molecular motion of the trapped radicals[12] constitute the cause for the formation of a long chain graft. At a higher reaction time (say, 7 h) molecular weight is comparatively lower than when the reaction time is low. However, when the reaction time is increased, the extent of grafting increases. From our earlier results[8] it is observed that radical sites do not increase continuously with reaction time, and after a certain time interval (e.g., 1 hour), the number of active sites remains constant. With the increase of reaction time the chain length would grow, but this will be opposed by

TABLE I
Effect of Various Grafting Parameters on the Molecular Weight of the Branched Polystyrene Chain

Grafting conditions				Molecular weight $\times 10^{-5}$			
Solvent composition	Temperature (°C)	Reaction time (h)	% of Grafting	Number average (Mn)	Weight average (Mw)	Z average (Mz)	Polymer dispersity (Mw/Mn)
1: Effect of Temperature							
50% MeOH + 50% H_2O	45	5	17.1	2.14	3.64	4.69	1.70
	55	5	38.6	2.34	4.32	6.00	1.84
2: Effect of Reaction Time							
50% MeOH + 50% H_2O	55	½	9.0	2.52	6.84	9.25	2.72
	55	5	38.6	2.34	4.32	6.00	1.84
	55	7	41.1	1.74	3.91	4.40	2.25
3: Effect of Solvents as well as composition of the Solvent							
30% MeOH + 70% H_2O	50	5	20.2	2.30	4.32	7.46	1.90
50% MeOH + 50% H_2O	50	5	35.9	3.52	5.29	7.86	1.50
70% MeOH + 30% H_2O	50	5	18.1	2.96	7.46	9.67	2.52
40% EtOH + 60% H_2O	50	5	24.3	7.16	11.08	14.49	1.55
70% EtOH + 30% H_2O	50	5	6.1	2.67	10.32	14.07	3.86
50% BuOH + 50% H_2O	50	5	6.9	5.84	10.52	12.39	1.81

TABLE II
Effect of Various Grafting Parameters on the Molecular Weight of the Branched Polystyrene Chain Where Grafting is Carried Out from a Monomer Mixture of Styrene and Acrylamide

Composition of		Grafting conditions		% of Grafting			Molecular weight $\times 10^{-5}$			
Solvent	Monomer acrylamide: styrene	Temperature (°C)	Reaction time (h)	Total	Styrene	Acrylamide	Number average (Mn)	Weight average (Mw)	Z-average (Mz)	Polymer dispersity (Mw/Mn)
1: Effect of Temperature and Reaction time										
50% MeOH +	1:1	45	2	6.0	2.3	3.7	1.29	5.08	8.32	3.94
50% H_2O	1:1	50	2	10.6	6.8	3.8	1.75	3.79	5.66	2.16
	1:1	55	2	23.9	20.3	3.6	2.65	4.47	6.73	1.69
	1:1	45	4	15.9	11.0	4.9	1.82	4.71	6.26	2.59
	1:1	50	5	33.9	28.3	5.6	2.87	5.08	8.27	1.76
	1:1	45	7	17.4	13.3	4.1	3.12	5.64	7.17	1.80
	1:1	50	7	38.6	33.8	4.8	2.00	3.82	5.15	1.91
	1:1	55	7	54.3	47.6	6.7	2.84	4.39	5.70	1.54
2: Effect of Monomer Composition in Solution										
50% MeOH +	1:4	50	2	11.5	7.5	4.0	2.08	6.81	7.24	3.27
50% H_2O	1:8	50	2	10.0	6.8	3.2	2.03	3.49	4.79	1.71
	1:4	50	4	23.4	18.5	4.9	2.20	3.95	5.34	1.80
	4:1	50	4	20.4	15.1	5.3	1.49	4.21	5.78	2.83
	1:4	50	7	36.1	28.7	7.4	2.12	4.46	5.02	2.10
	1:8	50	7	32.5	28.1	4.4	3.46	5.32	7.18	1.53

the degradation of the polymer chain when passed through the GPC column.[13] This may constitute the answer to why the molecular weight of the graft decreases though the extent of grafting increases when the reaction time is increased.

From Table I, it is further evident that the molecular weight distribution is also affected on changing the solvent composition. This is in fact, corroborated by our earlier observation.[9] In methanol–water system having a composition of 1:1 maximum grafting takes place due to Trommsdorff-type effect and this leads to a higher molecular weight material having polymer dispersity ratio close to 1.5. In ethanol–water system ethanol is a poor swelling agent and at the same time the hydrogen abstraction rate constant of this alcohol is greater than methanol; this leads to a low percent add on. But the molecular weight of the graft in ethanol is found to be much larger and is almost as large as that observed in butanol medium. The large molecular weight in case of butanol as solvent can be explained by the low chain transfer property associated with its lower hydrogen abstraction ratio although it is a poor swelling agent. However, the observed higher molecular weight in the case of ethanol as solvent is not clear. This may arise from a longer life time of the growing radical in order that smaller numbers of growing chains which survived after overcoming the detrimental effects lead to higher molecular weight.

When two monomers (e.g., styrene and acrylamide) are grafted simultaneously to cellulose acetate, the molecular weight data are shown in Table II. From this table when one considers the effect of temperature at a particular reaction time, molecular weight is found to increase with the increase of temperature whereas polymer dispersity ratio at the same time decreases; but this trend is not valid for higher reaction time, say for 7 h. For a particular temperature molecular weight increases with the increase in reaction time but polymer dispersity ratio at first decreases and then increases. The mode of variation of molecular weight and polymer dispersity is similar to that of the single-component system. The reason of such variation is therefore similar to that discussed earlier when only styrene is grafted to cellulose acetate.

With the change in composition of monomers (as shown in Table II), molecular weight is observed to be larger in case of a greater styrene content in the monomer mixture. When the concentration of styrene in the mixture is less than that of acrylamide, polymer dispersity is found to increase. We have reported earlier[8] by the bromine-labelling method that the styrene-type graft radicals are longer lived than the acrylamide-type ones. Therefore, molecular weight increases with the increase of styrene content in the medium, whereas it decreases with the increase of acrylamide content in the medium. Due to short-lived acrylamide-type graft radicals, the broadening of molecular weight distribution is observed when the concentration of acrylamide is increased.

From Tables I and II, as well as from our earlier observation,[9] it is observed that in the single-component system, the extent of grafting is found to be less than in the corresponding concentration of the two-component system, but molecular weight data show the reverse behavior. During the acid hydrolysis of the grafted copolymer, the acrylamide residues are de-

stroyed because grafted copolymers in which only acrylamide is grafted give no residue after similar treatment. Due to the destruction of the acrylamide portions in the chain containing styrene-acrylamide copolymer as well as the poly-acrylamide homopolymer, the grafted chains are broken whence the chains become shorter, as a result of which various short chains appear, and hence, polymer dispersity increases. When reaction time is increased, the degradation of the main chain may occur, whence the situation becomes more complex.

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