International Journal of Education and Science Research Review
E-ISSN 2348-6457
Volume-2, Issue-4 August- 2015
www.ijesrr.org Email- editor@ijesrr.org

Optimization Condition of Grafting of Polyvinylidene Fluoride Film by Methyl 2-Methylpropenoate Using Benzoyl Peroxide as Initiator

Pravin Kumar[1*], Rajeev. K. Gupta[2], Rishi Deewan[2]
[1*]Department of Physics, Singhania University, Pacheri Bari,
Jhunjhunu, Rajasthan, India.
[1*]Email: pravin.phy999@gmail.com
[2]Department of Physics, University of Petroleum and Energy studies Bidholi,
Dehradun, Uttarakhand, India.

ABSTRACT:
In this work the optimum condition of grafting of PVDF film has been achieved by changing monomer concentration, molarity of initiator, temperature of reaction and time of reaction. The study reveals that grafting of PVDF film by methyl 2-methylpropenoate using benzoyl peroxide as initiator has modified the surface roughness enhancing the contact angle of surface for pure water. The maximum value of degree of grafting was recorded 7.70% for initiator molarity .03M, monomer concentration 15%, temperature of reaction 60 degree Celsius, and time of reaction 60 minutes. Goniometric measurements of pristine and grafted PVDF film were recorded.

KEYWORDS: Grafting, concentration, contact angle, pristine.

1. INTRODUCTION:

The term polymer[1-2] was pronounced first time in 1886 when Berthelot found that "styrene heated at 200 degree Celsius, changes itself into a resinous polymer''.The concept of polymers in the sense we use today Was proposed by Hermann Staudinger which lead to the Nobel Prize in 1953 for his research work [3]. Elastomers (rubbers), Plastics and fibers have made the human life more dependable on polymers. Macromolecular science has had a major impact on the way we live. It is difficult to find an aspect of our lives that is not affected by polymers. Just 60 years ago, materials we now take for granted were non-existent. With further advances in the understanding of polymers, and with new applications being researched, there is no reason to believe that the revolution will stop any time soon. Polyvinylidene fluoride (PVDF) films [4] are light, flexible, and have high piezoelectricity. Because of these advantages, they have been widely used as sensors in applications such as underwater measurements, nondestructive damage detection, robotics, and active vibration suppression. Western transfers are an important tool for proteomics research, diagnostics, and forensics applications. They are widely used to detect the presence of proteins in unknown or complex sample mixtures, as well as determine the relative abundance of specific proteins. The physical characteristics of PVDF membrane, such as durability during stripping and high tensile strength for ease of handling, make it an excellent choice for protein detection. The hydrophobic nature of fluorine based polymers have opened a variety of applications such as antibiofouling paints for under water vehicles, self-cleaning windshields for automobiles. Wenzel and Cassie-Baxter [5] theories have shown that hydrophobicity ($CA>90^o$) is directly related to the nanoscale roughness of the surface. The survey of literature shows that the modification of surface roughness of PVDF film by thermal process is rare. In this work we have recorded an increase in contact angle for pure water on grafted PVDF film. The maximum grafting of film was achieved by changing different parameters [6].

2. EXPERIMENTAL:

Polyvinylidene fluoride (PVDF) film (.175mm thickness) was obtained from Good Fellow, Cambridge Limited of Huntingdon (England). Benzoyl peroxide was purchased from SD Fine chemicals (India). 2-methylpropenoate and acetone were obtained from Merck chemicals (India).PVDF film was washed by acetone and dried in an oven. Double distilled water was used as the reaction medium for copolymerization. The film was cut into small pieces of area ranging from $2cm^2$ to $4\ cm^2$. The pieces were weighed by a digital balance of least count .0001gm. Weighed PTFE film was placed in a standard three necked flask fitted with water condenser and thermometer . A definite amount of water (20-35 ml) was added, followed by the addition of a known amount of 2-methylpropenoate (5%-20%V/V) and BPO (.01M-.03M) taken in definite proportions. The mixture was heated for definite time intervals. The grafted film was dried and weight was recorded. The optimum condition of grafting was obtained by changing monomer concentration, molarity of initiator, temperature of reaction, and time of reaction**.**

3. RESULTS AND DISCUSSION:

The rate of grafting depends on various parameters such as monomer concentration, initiator molarity, reaction temperature and time of reaction. The degree of grafting was calculated according to the following expression

$$G\% = (W_G - W_P)\ x100/W_P$$

Where W_G and W_P are the weights of grafted PVDF film and pristine film [7]. The results of grafting have been given in tables 1-4.

3.1GRAFTING VARIATION WITH INITIATOR (BPO) MOLARITY:

The degree of grafting increases to a maximum value of 7.70%with the increase in initiator molarity up to .03M and then decreases. When the concentration of the BPO exceeds a certain value, increased free radical concentration results in serious homopolymerization and decreases the rate of grafting [8]. The variation of grafting percentage with initiator molarity is shown in figure 1.

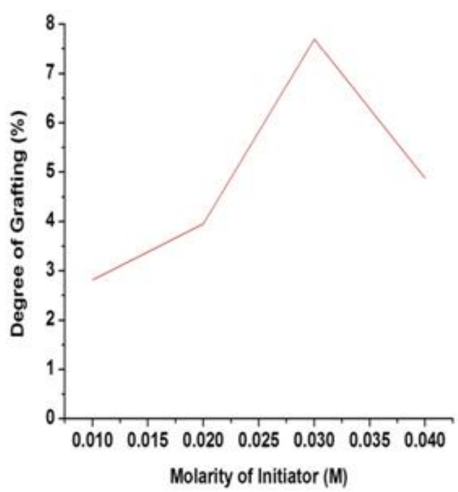

Figure 1: Variation of grafting percentage with Initiator molarity.

3.2 GRAFTING VARIATION WITH MONOMER CONCENTRATION:

The grafting percentage increases initially with monomer concentration up to 15% and then decrease on further increase in concentration of methyl 2-methylpropenoate. At higher concentrations of monomer the free radical sites at PVDF backbone decrease reducing the degree of grafting. The variation of grafting percentage with monomer concentration has been plotted in figure 2 for initiator molarity of .03M. The maximum values of grafting percentage for monomer concentrations 10%, 15%, 20% have been taken for plotting of graph.

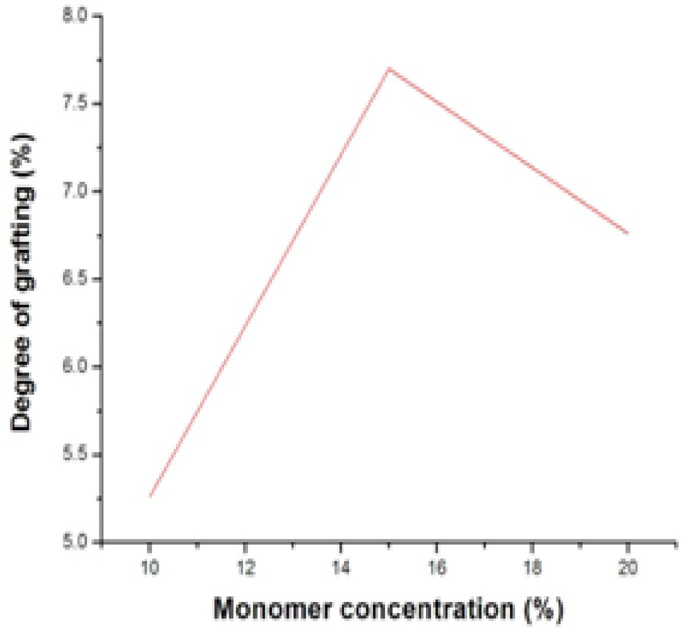

Figure 2: Variation of grafting percentage with monomer concentration.

3.3 GRAFTING VARIATION WITH TEMPERATURE OF REACTION:

The temperature of reaction is a key parameter in grafting process. The weights of grafted films were taken for temperature range from 50^0C to 80^0C.It is found that the grafting percentage increases up to 60^0C and then decreases gradually. This may be due to the increase in initiation and propagation rates of copolymerization or due to increase in the decomposition of the initiator leading to the formation of more free radicals and the generation of active sites on the polymeric backbone. However beyond optimum temperature, the grafting rate decreases because the growing polymeric chains are terminated and the chain transfer reactions are occurred. The variation of grafting percentage with temperature is shown in figure 3 for initiator molarity .03 M and monomer concentration 15%.

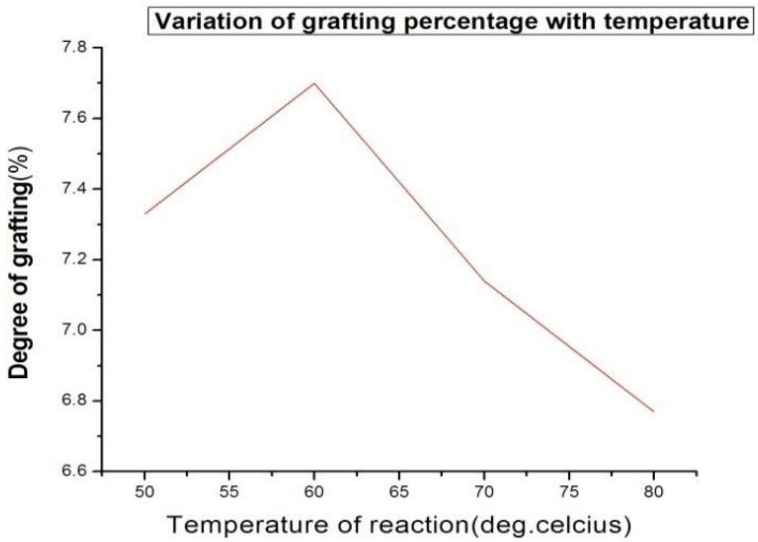

Figure 3: Variation of grafting percentage with temperature.

3.4 GRAFTING VARIATION WITH TIME OF REACTION:

The degree of grafting is also affected by reaction time. The grafting percentage is found maximum for reaction time of 60 minute. It is due the decreasing of concentration of initiator for higher time of reaction. The variation of grafting percentage with reaction time is shown in figure 4 for initiator molarity .03M, monomer concentration 15%.

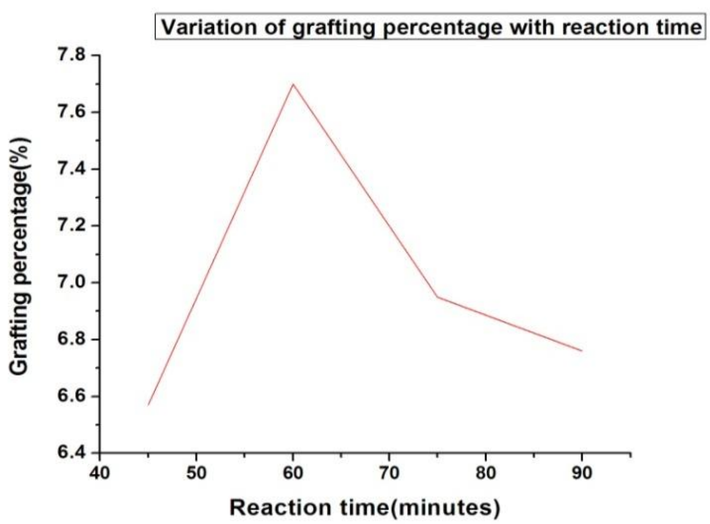

Figure 4: Variation of grafting percentage with reaction time.

3.5 CONTACT ANGLE ANALYSIS:

The contact angle of pristine PVDF film was measured using drop shape analyzer- 25. The syringe volume of water drop was kept at minimum level to minimize the effect of gravity on drop shape. The contact angle of pure water on pristine PVDF film was recorded 63.8 degree. The contact angles for grafted samples of film were recorded for monomer concentration 10%to20%, temperature of reaction 60^0C and time of reaction 60 minutes. It is found that maximum contact angle 81.6^0 is for film grafted at monomer molarity of .03M, monomer concentration 15%, time of reaction 60 minutes and temperature of reaction 60^0C. The shapes of water drops on pristine and maximum grafted PVDF films are shown in figure 5 and figure 6.The variation of contact angle with monomer concentration is shown in figure 7.

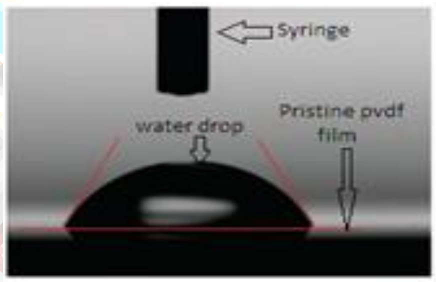

Figure 5.Goniometric image of water drop on grafted PVDF film

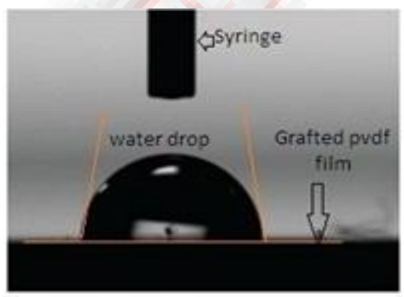

Figure 6.Goniometric image of water drop on pristine PVDF film.

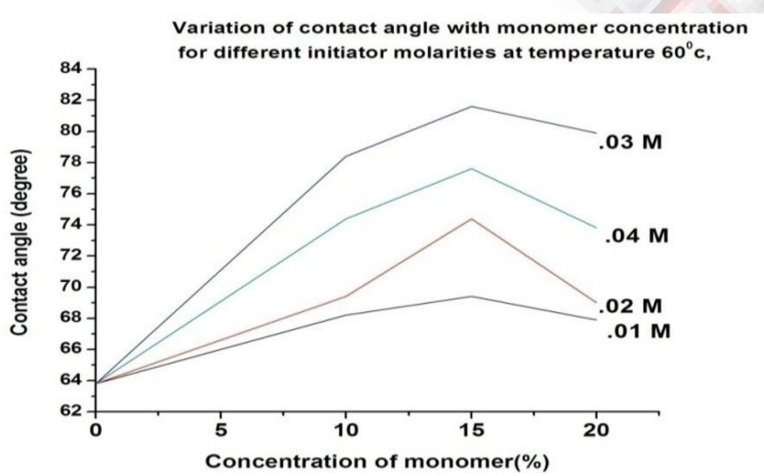

Figure 7.Variation of contact angle with monomer concentration

International Journal of Education and Science Research Review
Volume-2, Issue-4 August- 2015 E- ISSN 2348-6457
www.ijesrr.org Email- editor@ijesrr.org

Table 1: Grafting results of PVDF film for BPO molarity .01 M

BPO MOLARITY (M)	MMA CONCENTRATION (%)	CONT ANGLE OF PRISTIN-E FILM (DEG)	WEIGHT OF PRISTINE FILM (gm)	REACTION TIME(MIN)	TEMPER-ATUR E (^{0}C)	WEIGHT OF GRAFTED POLYMER (gm)	GRAFTING %	CONT. ANGLE (DEG.) GRAFTED FILM
.01M	**10%**	63.8^0	.0532	45	50	.0533	.187	
					60	.0536	.751	
					70	.0535	.563	
					80	.0534	.357	
			.0532	60	50	.0540	1.50	
					60	**.0541**	**1.69**	**68.2^0**
					70	.0538	1.12	
					80	.0537	.939	
			.0531	75	50	.0538	1.44	
					60	.0539	1.46	
					70	.0536	.941	
					80	.0535	.753	
			.0532	90	50	.0534	.357	
					60	.0536	.752	
					70	.0535	.564	
					80	.0533	.187	
	15%	63.8^0	.0532	45	50	.0533	.187	
					60	.0538	1.12	
					70	.0536	.751	
					80	.0535	.563	
			.0531	60	50	.0543	2.25	
					60	**.0546**	**2.82**	**69.4^0**
					70	.0544	2.44	
					80	.0542	2.07	
			.0532	75	50	.0539	1.31	
					60	.0542	1.87	
					70	.0538	1.12	
					80	.0537	.939	
			.0532	90	50	.0536	.751	
					60	.0537	.939	
					70	.0534	.357	
					80	.0533	.187	
	20%	63.8^0	.0532	45	50	.0538	1.12	
					60	.0539	1.31	
					70	.0537	.939	
					80	.0536	.751	
			.0532	60	50	.0539	1.31	
					60	**.0540**	**1.50**	**67.9^O**
					70	.0537	.939	
					80	.0535	.564	
			.0532	75	50	.0538	1.12	
					60	.0539	1.31	
					70	.0536	.751	
					80	.0537	.939	
			.0532	90	50	.0535	.563	
					60	.0537	.939	
					70	.0534	.375	
					80	.0533	.187	

Table 2: Grafting Results of PVDF film for BPO molarity .02 M

BPO MOLARITY (M)	MMA CONCENTRATION (%)	CONT ANGLE OF PRISTINE FILM (DEG)	WEIGHT OF PRISTINE FILM (gm)	REACTION TIME(MIN)	TEMPERATURE (^{0}C)	WEIGHT OF GRAFTED POLYMER (gm)	GRAFTING %	CONT. ANGLE (DEG.) GRAFTED FILM
.02M	10%	63.8^0	.0532	45	50	.0542	1.87	
					60	.0544	2.25	
					70	.0540	1.50	
					80	.0539	1.31	
			.0532	**60**	50	.0546	2.63	
					60	**.0547**	**2.81**	**69.4^0**
					70	.0545	2.44	
					80	.0544	2.25	
			.0532	75	50	.0540	1.50	
					60	.0545	2.44	
					70	.0542	1.87	
					80	.0540	1.50	
			.0532	90	50	.0542	1.87	
					60	.0543	2.06	
					70	.0541	1.69	
					80	.0539	1.31	
	15%	63.8^0	.0532	45	50	.0548	3.00	
					60	.0550	3.38	
					70	.0547	2.81	
					80	.0546	2.63	
			.0531	60	50	.0551	3.76	
					60	**.0552**	**3.95**	**74.4^0**
					70	.0551	3.76	
					80	.0547	2.81	
			.0532	75	50	.0548	3.00	
					60	.0550	3.38	
					70	.0546	2.63	
					80	.0545	2.44	
			.0532	90	50	.0544	2.25	
					60	.0545	2.44	
					70	.0543	2.06	
					80	.0542	1.87	
	20%	63.8^0	.0532	45	50	.0539	1.31	
					60	.0541	1.69	
					70	.0538	1.12	
					80	.0536	.751	
			.0531	60	50	.0544	2.44	
					60	**.0545**	**2.63**	**69^0**
					70	.0542	2.07	
					80	.0540	1.69	
			.0532	75	50	.0538	1.12	
					60	.0539	1.31	
					70	.0535	.563	
					80	.0534	.375	
			.0532	90	50	.0534	.375	
					60	.0536	.751	
					70	.0534	.375	
					80	.0533	.187	

International Journal of Education and Science Research Review
Volume-2, Issue-4 August- 2015 E- ISSN 2348-6457
www.ijesrr.org Email- editor@ijesrr.org

Table 3: Grafting Results of PVDF film for BPO molarity .03 M

BPO MOLARITY (M)	MMA CONCENTRATION (%)	CONT ANGLE OF PRISTINE FILM (DEG	WEIGHT OF PRISTINE FILM (gm)	REACTION TIME(MIN)	TEMPERATURE (^{0}C)	WEIGHT OF GRAFTED POLYMER (gm)	GRAFTING %	CONT. ANGLE (DEG.) GRAFTED FILM
.03M	10%	63.8^0	.0532	45	50	.0552	3.75	
					60	.0558	4.88	
					70	.0551	3.57	
					80	.0548	3.00	
			.0532	**60**	50	.0555	4.32	
					60	**.0560**	**5.26**	**78.4^0**
					70	.0556	4.51	
					80	.0552	3.75	
			.0532	75	50	.0549	3.19	
					60	.0550	3.38	
					70	.0548	3.00	
					80	.0546	2.63	
			.0532	90	50	.0548	3.01	
					60	.0549	3.19	
					70	.0548	3.01	
					80	.0545	2.44	
	15%	63.8^0	.0532	45	50	.0564	6.01	
					60	.0567	6.57	
					70	.0558	4.88	
					80	.0550	3.38	
			.0531	60	50	.0571	7.33	
					60	**.0573**	**7.70**	**81.6^0**
					70	.0570	7.14	
					80	.0567	6.77	
			.0532	75	50	.0568	6.76	
					60	.0569	6.95	
					70	.0566	6.39	
					80	.0564	6.01	
			.0532	90	50	.0565	6.20	
					60	.0568	6.76	
					70	.0563	5.82	
					80	.0560	5.26	
	20%	87.5^0	.0532	45	50	.0564	6.01	
					60	.0565	6.20	
					70	.0562	5.63	
					80	.0558	4.88	
			.0531	60	50	.0567	6.57	
					60	.0568	6.76	79.9^0
					70	.0564	6.01	
					80	.0561	5.64	
			.0532	75	50	.0558	4.88	
					60	.0560	5.26	
					70	.0557	4.69	
					80	.0555	4.32	
			.0532	90	50	.0556	4.51	
					60	.0558	4.88	
					70	.0556	4.51	
					80	.0554	4.13	

Table 4: Grafting Results of PVDF film for BPO molarity .04 M

BPO MOLARITY (M)	MMA CONCENTRATION (%)	CONT ANGLE OF PRISTIN-E FILM (DEG	WEIGHT OF PRISTINE FILM (gm)	REACTION TIME(MIN)	TEMPERATURE (^0C)	WEIGHT OF GRAFTED POLYMER (gm)	GRAFTING %	CONT. ANGLE (DEG.)
.04M	10%	63.8^0	.0532	45	50	.0552	3.75	
					60	.0554	4.13	
					70	.0550	3.38	
					80	.0549	3.19	
			.0531	60	50	.0553	4.14	
					60	**.0555**	**4.52**	**74.4^0**
					70	.0554	4.33	
					80	.0553	4.14	
			.0532	75	50	.0548	3.01	
					60	.0549	3.19	
					70	.0544	2.25	
					80	.0543	2.06	
			.0532	90	50	.0544	2.25	
					60	.0545	2.44	
					70	.0543	2.06	
					80	.0540	1.50	
	15%	63.8^0	.0532	45	50	.0553	3.94	
					60	.0554	4.13	
					70	.0551	3.57	
					80	.0550	3.38	
			.0532	60	50	.0554	4.13	
					60	**.0558**	**4.88**	**77.6^0**
					70	.0553	3.94	
					80	.0552	3.75	
			.0532	75	50	.0550	3.38	
					60	.0551	3.57	
					70	.0546	2.63	
					80	.0543	2.06	
			.0532	90	50	.0549	3.19	
					60	.0551	3.57	
					70	.0546	2.63	
					80	.0544	2.25	
	20%	63.8^0	.0532	45	50	.0551	3.57	
					60	.0552	3.75	
					70	.0550	3.38	
					80	.0549	3.19	
			.0532	60	50	.0550	3.38	
					60	**.0553**	**3.94**	**73.8ss^0**
					70	.0551	3.57	
					80	.0547	2.81	
			.0532	75	50	.0548	3.01	
					60	.0549	3.19	
					70	.0548	3.01	
					80	.0545	2.44	
			.0532	90	50	.0545	2.44	
					60	.0548	3.01	
					70	.0544	2.25	
					80	.0540	1.50	

4. CONCLUSION:

The optimum conditions for grafting of PVDF film are obtained for monomer concentration 15%, initiator molarity .03M, temperature of reaction 60^0C and time of reaction 60 minutes. It is observed that contact angle also increases with the increase in grafting percentage of film. The contact angle of pristine film is found 63.8^0 and 81.6^0 for maximum grafted film. The study reveals that contact angle is also affected by temperature of reaction, concentration of reaction, molarity of initiator and time of reaction. The increase in hydrophobicity opens wide applications in making self-cleaning surfaces in automobile, glass industries and in underwater measurements.

5. REFERENCES:

1. Drumond C. J. ,Vasic Z.R. ,Geddes N., Jurich M.C.,Chatelier R. C.,Gengenbach T.R., Griesser H.J.,(1997) Colloids Surface: Physicochem Eng. Aspects, 117,119.
2. Steve Rannard : Introduction to Polymer Sciences.
3. "Hermann Staudinger: Foundation of Polymer Science". *National Historic Chemical Landmarks*, American Chemical Society 2012.
4. Zhang, Qiwu; Lu, Jinfeng; Saito, Fumio; Baron, Michel (2001). "Mechanochemical solid-phase reaction between polyvinylidene fluoride and sodium hydroxide". *Journal of Applied Polymer Science* **81** (9): 2249.
5. T. S. Chow (1998). "Wetting of rough surfaces". *Journal of Physics: Condensed Matter* 10 (27):L445.Bibcode:1998JPCM...10L.445C. doi:10.1088/0953-8984/10/27/001
6. Feng, Chun; Li, Yongjun; Yang, Dong; Hu, Jianhua; Zhang, Xiaohuan; Huang, Xiaoyu (2011). "Well-defined graft copolymers: from controlled synthesis to multipurpose applications". *Chemical Society Reviews* 40 (3): 1282.
7. Jingxin Lei[a*], Qiman Li[a] & Guangjian He[a] pages 51-57 . DOI: 10.1081/PPT- 120002059 Published online: 15 Aug 2006"Accuracy measurement of grafting degree of radiation-induced surface graft polymerization by weighing".
8. Principles of Polymerization, Fourth Edition. By George Odian ISBN 0-471-27400-3 John Wiley & Sons, Inc