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İsmet Kaya[a]; Eyüp özdemir[b]
[a] Department of Chemistry, K. Maraş Sütçü İmam University, K. Maraş, Turkey [b] Department of Chemistry, Firat University, Elazi, Turkey

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THERMODYNAMIC INTERACTIONS AND CHARACTERIZATION OF POLY(ETHYL METHACRYLATE) BY INVERSE GAS CHROMATOGRAPHY

İsmet Kaya
Department of Chemistry, K.Maraş Sütçü İmam University,K.Maraş,Turkey
Eyüp Özdemir
Department of Chemistry, Fırat University, Elazığ,Turkey

ABSTRACT

The inverse gas chromatography (i.g.c.)method was applied to poly(ethyl methacrylate) (PEMA)as a method for polymer characterization and thermodynamic interactions. We have shown that the method was useful in obtaining meaningful thermodynamic data on PEMA-solvent systems. Five different families with different chemical nature and polarity were used to obtain some insights about PEMA-solvent interactions. PEMA was found to decompose above 210 °C (determined by TGA). The PEMA-solvent interaction parameters and the free energy of mixing were determined at a series of temperature.The glass transition temperature (Tg), of PEMA was found about 70 °C .The thermodynamic sorption functions for the sorption process of the different chemical nature of probes into PEMA solution were obtained and discussed in terms of their interactions with PEMA.Furthermore, the contributions of CH_2 ,C= O,C= O- OR,aromatic and OH functional groups in the five series to the sorption process were also obtained.We found that the formation of hydrogen bond between the C= O group of PEMA and the OH group of the alcohol is stronger than the dipole-dipole interactions between PEMA and the carbonyl groups of at the acetate and ketone and the dispersive forces between PEMA and the alkanes.Acetates and ketones were found to be good solvents and weak solvents respectively PEMA. Alkanes, o-xylene and methanol were found to be non-solvents of PEMA.

Keywords: Thermodynamic parameters,Poly(ethyl methacrylate), inverse gas chromatography.

INTRODUCTION

The inverse gas chromatography (i.g.c.) method has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymeric materials and to investigate polymer-polymer miscibility[1-5]. The term "inverse" indicates that the polymeric stationary phase of the chromatographic column is of interest in contrast to conventional gas chromatography. The chromatographic column in this work contains the polymer under study. Because of the high viscosity of polymers,the existing methods for the characterization of polymers are best by a number of technical difficulties. The i.g.c. method is a reliable method for the characterization of amorphous and semicrystalline polymers. The i.g.c. method is simple, fast, economical, and provides valuable thermodynamic information for characterization of polymeric substances.

The i.g.c. method was developed by Smidsrod and Guillet [6] and was applied to many polymeric systems. It has been shown that the i.g.c. method yields information on polymer-solvent and polymer-polymer systems such

as solubility parameters, interaction parameters, diffusion constants,enthalpies of mixing,surface energies and areas,adsorption isotherms,glass transition temperatures, Tg melting point temperatures,Tm and degree of crystallinity. Furthermore, the i.g.c. method is capable of obtaining physicochemical properties, the structure and chemical interactions of macromolecules.[7-15]

In this paper, we have examine the application of the i.g.c. method to an amorphous PEMA in temperature range 50°C to 200°C.

DATA REDUCTIONS

The probe specific retention volumes, Vg° corrected to 0 °C were calculated from the standard chromatographic relation :[16]

$$Vg^{\circ} = \Delta t\, F\, J\, 273.2 / W\, T\, (K) \tag{1}$$

Where $\Delta t = tp - tg$ is the difference between the retention times of the probe, tp, and the methane tg, F is the flow rate of the carrier gas measured at work temperature T(K), W is the mass of the polymeric stationary phase and J is a correction factor for gas compressibility, defined by the following relation:

$$J = 3/2[\,(Pi/Po)^2 - 1 / (Pi/Po)^3 - 1] \tag{2}$$

Where Pi and Po are the inlet and outlet pressures, respectively.

The PEMA-solute interaction parameters, χ_{12} at infinite dilution of different solutes used in this work are defined by the following equation:

$$\chi_{12} = \mathrm{Ln}\,(273.2R\, v_2 / Vg^{\circ}\, V_1\, P_1^{\circ}) - 1 - P_1^{\circ}/RT\,(B_{11} - V_1) \tag{3}$$

Where R is the gas constant, v_2 is the molar volume (ml/gr) of PEMA, V_1 is the molar volumeof the solute, P_1° is the vapour pressure and B_{11} is the second virial coefficient of the solute in the gaseous state. V_1, P_1° and B_{11} were calculated at the column temperature.

The vapour pressure P_1° was calculated from the Antonie equation as follows:

$$\log P_1^{\circ} = A - B / (t + C) \tag{4}$$

Where t is the temperature (in °C) and the constants A,B and C [17]. Second virial coefficients B_{11}, were computed using the following equation .[18]

$$B_{11}/Vc = 0.430 - 0.886\,(Tc/T) - 0.694\,(Tc/T)^2 - 0.0375\,(n-1)\,(Tc/T)^{4.5} \tag{5}$$

Where Vc and Tc are the critical molar volume and the critical temperature of the solute, respectively, and n is the number of carbon atoms in the solute. The molar volumes of the solutes V_1, were calculated using:[17]

For $0.2 \leq Tr \leq 0.8$

$$Vr^{\circ} = 0.33593 - 0.33953\, Tr + 1.51941\, Tr^2 - 2.02512\, Tr^3 + 1.11422\, Tr^4 \tag{6}$$

For $0.8 < Tr < 1.0$

$$Vr^{\circ} = 1.0 + 1.3\,(1-Tr)^{1/2} \log(1-Tr) - 0.50879\,(1-Tr) - 0.91534\,(1-Tr)^2 \tag{7}$$

For $0.2 < Tr < 1.0$

$$\Gamma = 0.29607 - 0.09045\, Tr - 0.04842\, Tr^2 \tag{8}$$

$$V_1/V^R = Vr^{\circ}(Tr)\,[\,1 - w\,\Gamma\,(Tr)\,]\Gamma / Vr^{\circ}\,(Tr^R)\,[\,1 - w\,\Gamma\,(Tr^R)) \tag{9}$$

Where Vr° and Γ are functions of reduced temperature and w is the acentric factor, Tr is reduced temperature and $V^R = M/d$, M and d is the molecular weight of the solute and density and Tr^R is reduced referance temperature.

The molar heat (enthalpy) of sorption of probe absorbed by the PEMA (ΔH_1^s) is given by the following equation:

$$\Delta H_1^s = -R\, \partial \ln Vg^{\circ} / \partial\,(1/T) \tag{10}$$

Where Vg° is the probe specific retention volumes and T is the column temperature.

The average partial molar heat of mixing at infinite dilution of the probe was calculated as follows:

$$\Delta H_1^{\infty} = R\, \partial \ln(\Omega_1^{\infty}) / \partial\,(1/T) \tag{11}$$

Where (Ω_1^{∞}) is the weight fraction activity coefficient of the solute probe at infinite dilution which is calculated according to the following equation:[19]

$$\Omega_1^{\infty} = 273.2\, R / Vg^{\circ} P_1^{\circ} M_1 \exp\left[-P_1^{\circ} (B_{11} - V_1) / RT\right] \qquad (12)$$

Where P_1°, V_1 and B_{11} were defined in equation (3) and M_1 is the molecular weight of the probe.

The partial molar free energy of mixing at infinite dilution is calculated from the weight fraction activity coefficient of the solute as follows :

$$\Delta G_1^{\infty} = RT\ln \Omega_1^{\infty} \qquad (13)$$

Where RT is the usual meaning.

The partial molar free energy of sorption at infinite dilution is calculated as follows:

$$\Delta G_1^{s} = -RT\ln (M_1\, Vg^{\circ} / 273.2\, R) \qquad (14)$$

By incorporating equations (10) and (14) we calculated the entropy of sorption of solutes as follows:

$$\Delta G_1^{s} = \Delta H_1^{s} - T\Delta S_1^{s} \qquad (15)$$

EXPERIMENTAL

Materials

Eleven polar and non-polar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity.Octane,nonane,decane,undecane and dodecane were supplied from Aldrich Chemical Co.and methanol,acetone,ethyl methyl ketone,methyl acetate,ethyl acetate,o-xylene were supplied from Merck Chemical Co. as chromatographic grade. Poly(ethyl methacrylate) was supplied by Aldrich Chemical Co.in powder from.Its molecular weight was estimated from intrinsic viscosity,( )=0.46dl gr-1 in 2-butanone at room temperature,to be 215.000 using published Chinai and Samuels constants (a:0.79,K:0.00283 ml gr-1).Chromosorb W (45-60 mesh) was supplied from Sigma Chemical Co.

Instrumentation and procedure

A Shimadzu GC-14A model gas chromatography equipped with a dual flame ionization dedectors. FID was used in the analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Methane was used as a noninteracting marker to correct for dead volume in the column. The net retention time was determined from the positions of the peak maxima for methane and for the probe molecule at each temperature. Pressures at inlet and outlet of the column,read from a mercury manometer (mmHg) were used to compute corrected retention volumes by the usual procedures. Flow rate were measured from the end of the column with a soap bubble flow meter. A flow rate of about 20 ml/ min^{-1} was used throughout our experiment. Column was prepared with 2.1m. a spiral glass column,3.2mm ID. The spiral glass column was washed with methylene chloride and was annealed prior to use.A column packing material was prepared by coating 45-60 mesh size chromosorb W with PEMA 0.60000 gr. was dissolved in 50 ml of N,N-Dimethyl acetamide (Merck) and 6.00000 gr. of the solid supporting material was then added to this solution and stirred.The solvent was removed by continuous stirring and slow evaporation under partial vacum in a Rotavapor.The prepared material was packed into a spiral glass column (3.2mm I.D.x2.1m.).Column was conditioned at 80°C and fast carrier gas flow rate for 24h prior to use.Probes were injected onto the column with 1μl Hamilton syringes.Three consecutive injections were made for each probe at each set of measurements.An injection volume was selected 0.3μl.The retention times of the probes were measured by using chromatopac CR6A,Shimadzu.Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide.

DTA and TGA curves were obtained by using the Shimadzu DTA 50 and Shimadzu TGA 50H thermal analyzers in nitrogen current (50 ml min^{-1}) at a heating rate of 10°C min^{-1}.

RESULTS and DISCUSSION

The specific retention volumes (Vg° of 11 probes) were obtained by using one loading PEMA and at a series of temperature. Different chemical nature and polarity (n-alkanes,n-acetates,n-ketones,aromatic and alcohol) were selected for this study.The Vg° values of these probes were calculated according to equation (1). The specific retention volume data are essential in the determination of physicochemical or thermodynamic properties of a polymer by i.g.c. In order to obtain these data,it is necessary to know the amount of the polymer that has been coated onto the support,the gas flow rate,column pressures and temperature. The amount of injected sample also affects the retention volume.[5] The specific retention volumes (Vg°) are given in Table 1. Data in Table 1 for each probe is demonstrated such as in Figure 1.

Table 1.Changes in specific retention volumes as a function of temperature (cm^3/gr polymer).

T(K)	Meth.	Acet.	Met.Act.	Et.Act.	E.M.K	O-xyl.	n-Oct.	n-Non.	n-Dec.	n-Undec	n-Dodec.
323	26.04	19.13	18.64	25.30	36.43	162.61	7.71	22.09	104.96	182.00	208.46
333	22.72	16.66	17.05	22.17	31.29	140.26	6.29	17.16	85.74	152.19	178.67
343	9.32	8.84	11.83	17.46	22.52	105.68	5.51	12.72	54.48	100.68	136.54
353	11.17	12.25	12.14	14.94	22.75	106.88	12.41	26.21	60.48	103.16	136.78
363	8.38	9.73	9.92	15.23	18.67	87.04	11.36	21.30	47.78	85.89	118.73
373	6.70	8.18	8.06	12.28	14.95	71.39	10.54	19.52	39.22	71.99	100.58
383	5.83	6.47	6.98	9.82	11.46	56.93	9.73	17.42	31.54	59.51	82.96
393	4.76	5.69	5.79	8.22	9.56	46.27	9.27	15.93	25.74	51.14	71.52
403	4.30	5.09	5.03	7.05	8.37	36.31	8.53	11.61	21.54	39.26	60.92
413	4.07	4.79	4.66	6.17	7.15	28.16	7.21	11.24	18.13	29.66	48.79
423	3.80	4.36	4.28	5.45	6.00	21.83	6.20	9.30	14.27	22.67	34.06
433	3.55	3.98	3.96	4.68	5.23	15.91	5.39	7.68	11.57	17.71	29.50
443	3.35	3.75	3.72	4.33	4.76	13.20	4.93	6.74	9.62	14.18	21.06
453	3.08	3.53	3.48	4.03	4.42	11.71	4.49	5.90	8.85	11.41	16.90
463	2.92	3.33	3.30	3.74	4.00	10.68	4.18	5.32	8.03	9.68	13.48
473	2.75	3.07	3.08	3.34	3.62	8.41	3.79	4.73	6.09	8.00	11.02

Meth:Methanol,Acet:Acetone,Met Act:Methyl Acetate.Et.Act:Ethyl Acetate.E.M.K.:Ethyl methyl ketone, O-xyl:O-xylene, n-Oct: n-Octane, n-Non: n-Nonane, n-Dec: n-Decane.n-Undec: n-Undecane, n-dodec: n-Dodecane.

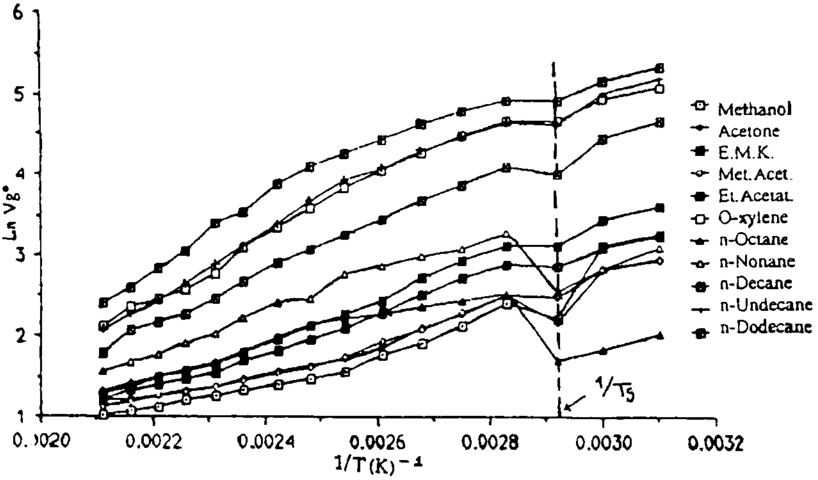

Figure 1.Changes in the specific retention volumes of the probes as a function of the inverse of temperature.

Table 2. PEMA-solute interaction coefficients χ_{12} and weight fraction activity coefficient Ω_1^{∞} of alkanes, acetates, ketones, o-xylene and methanol at 413-473K

	Ω_1^{∞}							χ_{12}						
Probes/ T(K)	413	423	433	443	453	463	473	413	423	433	443	453	463	473
Methanol	17.33	14.72	12.77	11.10	9.96	8.83	8.00	1.582	1.383	1.201	1.017	0.854	0.680	0.519
Acetone	10.04	9.22	8.47	7.69	7.07	6.51	6.25	0.932	0.805	0.673	0.528	0.394	0.253	0.156
E.M.K.	9.78	9.60	9.11	8.37	7.69	7.28	6.97	0.964	0.914	0.821	0.694	0.567	0.462	0.365
Met.Act.	8.26	7.52	6.89	6.33	5.86	5.42	5.10	0.717	0.580	0.443	0.313	0.183	0.048	-0.074
E.Act	8.67	8.10	7.82	7.14	6.57	6.08	5.95	0.820	0.716	0.636	0.502	0.369	0.236	0.133
O-Xyl.	8.87	8.82	9.52	9.22	8.36	7.53	7.95	0.987	0.962	1.019	0.965	0.841	0.710	0.734
Octane	20.17	18.53	17.05	15.22	13.82	12.41	11.57	1.744	1.631	1.514	1.366	1.230	1.080	0.966
Nonane	22.14	20.45	19.34	17.57	16.19	14.65	13.60	1.891	1.790	1.708	1.586	1.474	1.340	1.230
Decane	23.54	22.33	20.80	19.48	16.54	14.53	15.45	1.986	1.918	1.828	1.743	1.554	1.398	1.429
Undec.	24.79	23.46	22.18	20.89	20.00	18.38	17.53	2.062	1.995	1.925	1.849	1.787	1.681	1.609
Dodec.	26.02	26.40	21.80	22.53	20.95	20.01	19.04	2.126	2.131	1.930	1.951	1.864	1.802	1.734

Table 3. The partial molar free energies of mixing ΔG_1^{∞}(k.cal.mol^{-1}) and partial molar free energies ΔG_1^{s} (k.cal. Δmol^{-1}) alkanes, acetates, ketones, o-xylene and methanol at 413-473K and 353-403K by using PEMA of sorption as stationary phase.

	ΔG_1^{∞}							ΔG_1^{s}					
Probes/T(K)	413	423	433	443	453	463	473	353	363	373	383	393	403
Methanol	2.34	2.26	2.19	2.12	2.07	2.00	1.95	2.90	3.19	3.45	3.64	3.90	4.08
Acetone	1.89	1.87	1.84	1.80	1.76	1.72	1.72	2.84	3.08	3.30	3.56	3.76	3.94
E.M.K.	1.87	1.90	1.90	1.87	1.84	1.83	1.83	1.83	2.03	2.25	2.51	2.72	2.89
Met.Acet.	1.73	1.70	1.66	1.62	1.59	1.56	1.53	2.26	2.47	2.69	2.87	3.09	3.28
Et.Acetat.	1.77	1.76	1.77	1.73	1.69	1.66	1.68	1.86	2.03	2.25	2.48	2.68	2.87
O-xylene	1.79	1.83	1.94	1.96	1.91	1.86	1.95	0.48	0.64	0.80	1.00	1.19	1.41
n-Octane	2.47	2.45	2.44	2.40	2.36	2.32	2.30	1.94	2.05	2.17	2.29	2.38	2.51
n-Nonane	2.54	2.54	2.55	2.52	2.51	2.47	2.45	1.33	1.52	1.62	1.75	1.87	2.17
n-Decane	2.59	2.61	2.62	2.61	2.53	2.46	2.57	0.67	0.86	1.03	1.22	1.41	1.59
n-Undecane	2.64	2.65	2.66	2.68	2.70	2.68	2.69	0.23	0.37	0.51	0.67	0.81	1.04
n-Dodecane	2.67	2.75	2.65	2.74	2.74	2.76	2.77	0.03	0.07	0.20	0.35	0.48	0.61

Table 4.Partial molar heats of sorption ΔH_1^{s} (k.cal.mol^{-1}) of alkanes,acetates,ketones,o-xylene and methanol at temperature range 353-403K

Methanol	Acetone	E.M.K:	Met.acetate	Et.acetate	O-xylene	n-Octane	n-Nonane	n-Decane	n-Undec.	n-Dodec.
-5.38	-5.07	-5.90	-5.00	-5.46	-6.09	-2.08	-4.08	-5.87	-6.96	-9.45

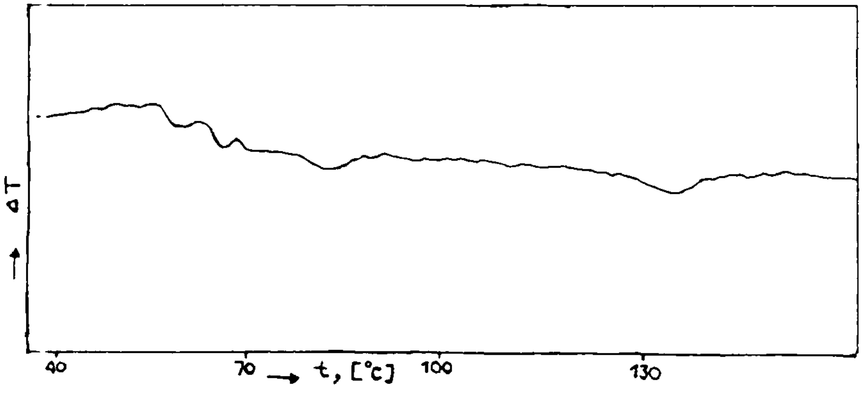

Figure 2. DTA curve of PEMA in nitrogen current (50ml min $^{-1}$) at a heating rate of 10°C min^{-1}

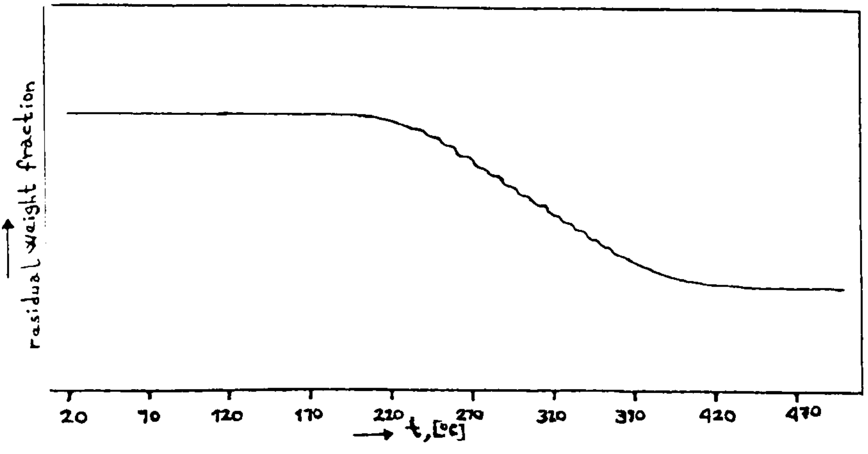

Figure 3. TGA curve of PEMA in nitrogen current (50 ml min^{-1})at a heating rate of 10 °C min $^{-1}$

As can be seen from Figure 1, the specific retention volumes of probes on PEMA are temperature dependent and decrease with the increase of temperature. The glass transition temperature of PEMA is found about 70°C, which is in agreement with the previous literature data[20]

PEMA-solvent interaction parameters,such as Flory-Huggins interaction parameter χ_{12} at infinite dilution of the probe,were calculated according to equation (3) in between 413K to 473K Generally, χ_{12} showed considerable dependence with change in the number of carbons and temperature at alkanes,ketones and acetates (Table 2.).A consequence from theoretical considerations is that χ_{12} has to be larger than 0.5 for the (polymer-nonsolvent) systems and smaller than 0.5 for the (polymer-solvent) systems.[21] The values of χ_{12} found in this experiment are high for alkanes, methanol and o-xylene,as usual for polymer-nonsolvent systems but are lowe for acetates and ketones as usual for PEMA-solvent systems.Similar results were obtained for the weight fraction activity coefficients (Ω_1^{∞}) and results listed in Table 2. We calculated the partial molar free energy of mixing (ΔG_1^{∞}) and partial molar free energies of sorption (ΔG_1^{s}) of probes according to equation (13),(14) and results listed inTable 3.

According to (Ω_1^{∞})data in Table 2. indicate that alkanes, methanol and o-xylene are bad solvent but acetates and ketones are moderate solvents for PEMA. The following rules have been formulated by Guillet.[22]

(Ω_1^{∞}) <5	good solvents
5 < (Ω_1^{∞}) <10	moderate solvents
(Ω_1^{∞})> 10	bad solvents

Partial molar heats of sorption ΔH_1^{s} for five families of probes into PEMA solution were calculated by using equation (10).Table 4.shows the calculated sorption function at temperature range 353-403K.Since the chemical nature and number of carbons of each probe are different from each other,the heat of sorption becomes more exothermic as more CH_2 groups are added to the three families of probes.The attraction forces between PEMA and acetates and ketones are actually a combination of two types:dispersive forces between the CH_2 groups of the acetates,ketones and the ethyl group of PEMA,and the interaction of the C= O groups of the acetates and ketones with the C= O groups of PEMA via dipole-dipole interactions.We calculated the contribution of the C= O groups of the acetates,ketones and the - OH group of the methanol to the sorption functions,by subtracting the contribution of alkanes and o-xylene sorption functions from that of the acetates,ketones and methanol (Table 3).The dipole-dipole interactions in PEMA-ketones and acetates systems are weaker than the hydrogen-bond interactions in PEMA-methanol system.

According to DTA analysis the glass transition temperature, Tg of PEMA has been found 64-65°C. Moreover according to GC analysis the glass transition temperature,Tg of PEMA has been found 70°C . DTA curve is shown in Figure 2. During TGA analysis, PEMA started to decompose above 210 °C (TGA curve, Figure 3).

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