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Physicochemical characterization of poly(*tert*-butyl acrylate-*b*-methyl methacrylate) prepared with atom transfer radical polymerization by inverse gas chromatography

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Abstract

Poly(*tert*-butyl acrylate) (P*t*BuA) was synthesized by atom transfer radical polymerization (ATRP) using methyl-2-bromo propionate (MBP) as an initiator in bulk at 80 °C. The successive ATRP of methyl methacrylate in diphenyl ether at 80 °C using previously obtained P*t*BuA as a macroinitiator led to formation of poly(*tert*-butyl acrylate-*b*-methyl methacrylate) (poly(*t*BuA-*b*-MMA)). The synthesized macroinitiator and block copolymer have controlled molecular weight and low polydispersity ($M_w/M_n < 1.2$). The block copolymer was characterized by gel permeation chromatography (GPC) and ^{1}H NMR. The retention diagrams of poly(*t*BuA-*b*-MMA) for some aliphatic esters and aromatic hydrocarbons were obtained using inverse gas chromatography (IGC) technique. The glass transition temperatures, T_gs of poly(*t*BuA-*b*-MMA) were determined by both differential scanning calorimeter (DSC) and IGC. It was observed that the block copolymer represents three T_gs at 50, 75 and 100 °C by IGC although it represents only one T_g at 71 °C by DSC. After the column was quenched from 180 to 0 °C, the T_g at 100 °C shifted to 105 °C however others did not change. Specific retention volumes, V_g^0 and the thermodynamical polymer–solvent interaction parameters such as Flory–Huggins, χ_{12}^∞, equation-of-state, χ_{12}^* and effective exchange energy, X_{eff} were found for all studied solvents. Partial molar heat of sorption, $\Delta\bar{H}_{1,\text{sorp}}$, partial molar heat of mixing, $\Delta\bar{H}_1^\infty$ and molar heat of vaporization, ΔH_v, were determined. In addition, the solubility parameter of the corresponding block copolymer, δ_2 was determined as 11.0 (cal/cm^3)$^{1/2}$ at 25 °C.

Keywords: Poly(*tert*-butyl acrylate-*b*-methyl methacrylate); ATRP; Inverse gas chromatography

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1. Introduction

Controlled/‘living’ radical polymerization includes a group of radical polymerization techniques that has attracted much attention over the past decade for providing simple and robust routes to the synthesis of well-defined, low polydispersity polymers. Among them, atom transfer radical polymerization (ATRP) is one of the most widely used living free radical polymerization technique [1–3]. This technique has been applied to prepare block copolymers with well-controlled molecular weights and well-defined structures [4]. For many applications, block copolymers are suitable materials because they allow different combinations of monomers and properties to be applied. Block copolymers of acrylates and methacrylates are synthetically interesting because of the morphological, phase, and mechanical properties of such polymers. These properties are realized partly through the combination of a high glass transition temperature (T_g) block (methacrylate) with a softer, lower T_g block (acrylate).

Inverse gas chromatography (IGC) is a gas phase technique to determine the physicochemical properties of the sample in the chromatographic column [5,6]. The principles of IGC are same as a conventional gas chromatographic (GC) experiment [7]. IGC is an extension of conventional GC in which a solid material to be investigated is immobilized within a column. Liquids of known properties are then injected into the column containing the sample. The retention times of these trace amount liquids are used in determination of their interactions

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with the solid in the column. This technique has been used extensively to study the interactions of both polymer–solvent and polymer–polymer [8,9]. Guillet established the foundations of the observation of the T_g by IGC technique [10,11]. After then, IGC is used to detect the thermal transition temperatures such as melting point (T_m), T_g, and other second order transition temperatures of the polymer. [8,12,13]. In this study, as a novel approach, microphase separation in the poly(*tert*-butyl acrylate-*b*-methyl methacrylate), poly(*t*BuA-*b*-MMA), diblock copolymer with a short P*t*BuA segment synthesized by ATRP were observed from the retention diagrams of the block copolymer with some aliphatic esters and aromatics by means of IGC technique. The branched and higher molecular weight aliphatic esters were selected to observe the thermal transitions of the copolymer at a wide temperature range. Aromatics and acetates with aliphatic side groups were selected to observe the effects of alkyl and chlorine substitutions on the interactions of solvent with ester group of the copolymer.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA; 99%, Aldrich) and *tert*-butyl acrylate (*t*BuA; 99%, Aldrich) were passed through basic alumina columns to remove inhibitors and then dried over CaH_2 and distilled in vacuo prior to use. Tetrahydrofuran (THF; 99.8%, J.T. Baker high pressure liquid chromatography grade) was dried and distilled over $LiAlH_4$. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA; Acros; >99%) was distilled (85–86 °C/12 mmHg). All other reagents were purchased from Aldrich and used as received.

Ethyl acetate (EA), propyl acetate (PA), isopropyl acetate (IPA) *n*-butyl acetate (BA), isobutyl acetate (IBA), *tert*-butyl acetate (*t*BA), isoamyl acetate (IAA), benzene (B), toluene (T), ethyl benzene (EB), *n*-propyl benzene (PB), isopropyl benzene (IPB) and chloro benzene (CB) were analytical reagent grade and used without further purification. Helium was used as carrier gas. The solvents and support material Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc.

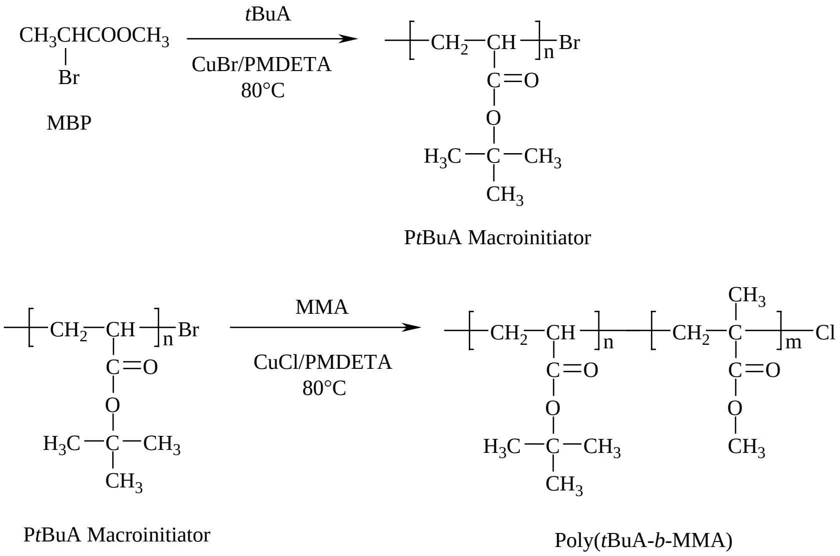
2.2. Instrumentation

The ^1H NMR spectra was recorded on a Bruker spectrometer (250 MHz for ^1H NMR) in $CDCl_3$. Gel permeation chromatography (GPC) measurements were performed with an Agilent model 1100 instrument consisting of pump and refractive-index and UV detectors and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was used as an eluent at a flow rate of 0.3 mL/min at 30 °C. The molecular weight of the polymers was calculated with the aid of polystyrene (PS) standards. All polymers obtained were dried under vacuum for 24 h, and conversions were determined by gravimetrically. DSC thermogram of poly(*t*BuA-*b*-MMA) block copolymer was recorded with Perkin–Elmer DSC 6 under nitrogen atmosphere.

A Hewlett–Packard 5890 Model, series II gas chromatograph with a thermal conductivity detector was used in this study. Data acquisition and analysis were performed by means of HP-3365 software. The column was stainless steel tubing with 3.2 mm OD and 1 m in length. The polymer was coated on the support by slowly evaporation of chloroform as stirring the Chromosorb-W in the polymer solution.

2.3. Synthesis of PtBuA and poly(tBuA-b-MMA) via ATRP

According to the procedure reported in the literature [14] the synthesis of P*t*BuA and poly(*t*BuA-*b*-MMA) are as follows: P*t*BuA macroinitiator was prepared by ATRP of *t*-BuA in bulk using CuBr/PMDETA as a catalyst and methyl-2-bromopropionate (MBP) as an initiator at 80 °C for a given time. To a Schlenk tube equipped with a magnetic stirring bar,



Scheme 1.

Table 1
Synthesis of poly(*t*BuA-*b*-MMA) diblock copolymer via ATRP–ATRP route

Run	Monomer	$[M]_0$ (mol/L)	Initiator	Time (min)	Conversion (%)	$M_{n,GPC}$[a]	Composition ^{1}H NMR	M_w/M_n
PI[b]	*t*BA	6.83	I	70	37	9000	–	1.14
PII[c]	MMA	4.67	PI	90	5	69,000	5% P*t*BuA, 95% PMMA	1.17

[a] Molecular weights were calculated by the aid of linear PS standards.

[b] $[M]_0:[I]_0:[CuBr]_0:[PMDETA]_0=100:1:1:1$, the polymerization was carried out at 80 °C.

[c] $[M]_0:[I]_0:[CuCl]_0:[PMDETA]_0=10000:1:1:1$ (MMA/DPE = 1 (v/v)), the polymerization was carried out at 80 °C.

the degassed monomer, ligand, catalyst, and initiator were added in the order mentioned. The tube was degassed by three freeze–pump–thaw cycles left under vacuum and placed in a thermostated oil bath. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated from excess of methanol/water (80/20; v/v). After decantation, the polymer was dissolved in a minimum amount of dichloromethane (approximately 30 mL) and dried over Na_2SO_4. Dichloromethane was then removed by evaporation.

Poly(*t*BuA-*b*-MMA) diblock copolymer was prepared in a Schlenk tube using a similar method to that employed in the preparation of P*t*BuA. In this case, bromo-terminated P*t*BuA was used as a macroinitiator, diphenylether (DPE) as solvent (MMA/DPE = 1; v/v), CuCl/PMDETA as the catalyst system. ATRP of MMA was carried out at 80 °C in an oil bath for the given time. After the purification procedure described in the preparation of macroinitiator, the resulting polymer was collected by precipitation into methanol/water (80/20; v/v), and then isolated by vacuum filtration.

2.4. Inverse gas chromatography theory

The specific retention volume, V_g^0 is determined experimentally from inverse gas chromatography measurements as follows [5–9].

$$V_g^0 = \frac{273.2Q(t_R - t_A)J}{(T_r w)} \tag{1}$$

where Q is carrier gas flow rate measured at the room temperature T_r; t_R and t_A are retention times of solvent and air, respectively; J is pressure drop correction factor which equals to $[3(p_i/p_o)^2 - 1]/[2(p_i/p_o)^3 - 1]$ where p_i and p_o are column inlet and outlet pressures, respectively, w is weight of polymer in the column.

According to the theories of Flory–Huggins and equation-of-state interaction parameters, χ_{12}^∞ and χ_{12}^* are defined in the Eqs. (2) and (3), respectively [15]:

$$\chi_{12}^\infty = \ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^0 V_1^0}\right) - 1 - p_1^0\left(B_{11} - V_1^0\right)/RT \tag{2}$$

where R is the universal gas constant; p_1^0, B_{11} and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T, v_2 is specific volume of the polymer, respectively.

$$\chi_{12}^* = \ln\left(\frac{273.2Rv_2^*}{p_1^0 V_g^0 V_1^*}\right) - 1 - p_1^0\left(B_{11} - V_1^0\right)/RT \tag{3}$$

where v_2^* is specific hard-core volume of the polymer and V_1^* is molar hard-core volume of the solvent.

The effective exchange energy parameter, X_{eff} in the equation of state theory is defined as follows,

$$RT\chi_{12}^* = p_1^* V_1^* \left\{3T_{1r} \ln\left[\frac{v_{1r}^{1/3} - 1}{v_{2r}^{1/3} - 1}\right] + v_{1r}^{-1} - v_{2r}^{-1}\right\} + X_{\text{eff}} V_1^* v_{2r}^{-1} \tag{4}$$

where p_1^* is characteristic pressure, v_{1r} and v_{2r} are reduced volume of the solvent and polymer, respectively. T_{1r} is reduced temperature of the solvent.

The partial molar heat of sorption, $\Delta\bar{H}_{1,\text{sorp}}$, of the solvent sorbed by the polymer, is given as [5–8]

$$\Delta\bar{H}_{1,\text{sorp}} = -R\left[\frac{\partial(\ln V_g^0)}{\partial(1/T)}\right] \tag{5}$$

where T is the column temperature (K) and the partial molar heat of mixing, $\Delta\bar{H}_1^\infty$ at infinite dilution of the solvent is given as

$$\Delta\bar{H}_1^\infty = R\left[\frac{\partial(\ln \Omega_1^\infty)}{\partial(1/T)}\right] \tag{6}$$

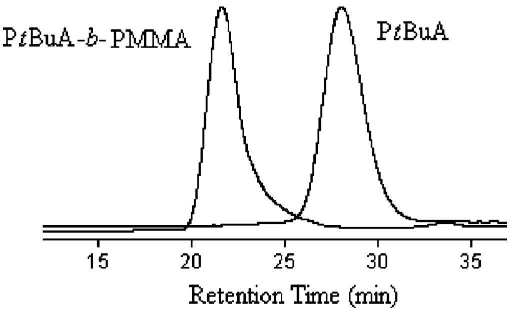


Fig. 1. GPC traces of P*t*BuA and poly(*t*BuA-*b*-MMA).

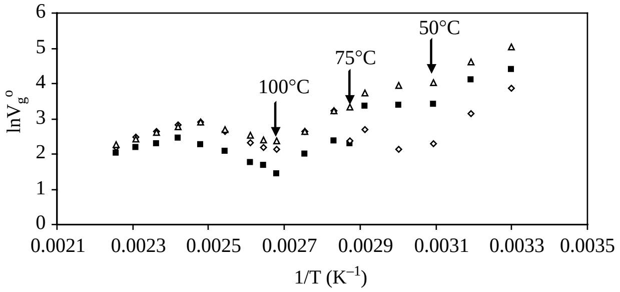


Fig. 2. Retention diagrams of BA (△), IBA (■) and *t*BA (◇) on poly(*t*BuA-*b*-MMA) before thermal process. Arrows indicate T_gs.

where Ω_1^∞ is the weight fraction activity coefficient of solvents at infinite dilution, defined by the following equation,

$$\ln \Omega_1^\infty = \ln\left(\frac{273.2R}{V_g^0 p_1^0 M_1}\right) - \frac{p_1^0(B_{11}-V_1^0)}{RT} \tag{7}$$

where M_1 is the molecular weight of solvent.

Molar heat of vaporization, ΔH_v, of the solvent is related to $\Delta\bar{H}_{1,\mathrm{sorp}}$ and $\Delta\bar{H}_1^\infty$ as follows:

$$\Delta H_v = \Delta\bar{H}_1^\infty - \Delta\bar{H}_{1,\mathrm{sorp}} \tag{8}$$

The solubility parameter of the polymer, δ_2 is found by combining of the Flory–Huggins and Hildebrand–Scathard theories [16,17]:

$$\left[\left(\frac{\delta_1^2}{RT}\right) - \left(\frac{\chi_{12}^\infty}{V_1^0}\right)\right] = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{\delta_2^2}{RT} \tag{9}$$

where δ_1 is solubility parameter of the solvent.

3. Results and discussions

The synthetic strategy followed for the preparation of poly(*t*BuA-*b*-MMA) block copolymer via the ATRP–ATRP route is depicted in Scheme 1. First, P*t*BuA homopolymer was synthesized via ATRP of *t*BuA in bulk at 80 °C using MBP as an initiator. Second, previously obtained P*t*BuA was used as a

Table 2
Specific retention volumes, V_g^0 (cm^3/g) of poly(*t*BuA-*b*-MMA) with the solvents given before (1) and after (2) thermal process

Solvents	140$^{(1)}$	150$^{(1)}$	150$^{(2)}$	160$^{(1)}$	160$^{(2)}$	170$^{(1)}$	170$^{(2)}$
EA	7.07	5.09	5.78	5.27	5.42	4.56	4.31
PA	10.62	8.84	8.21	7.54	7.86	6.60	6.66
IPA	7.03	6.44	5.45	4.88	5.06	4.15	4.63
BA	16.02	13.77	11.12	11.17	10.42	9.74	9.40
IBA	11.74	9.83	9.55	8.89	8.49	7.50	7.42
*t*BA	17.07	14.09	11.62	11.81	10.91	8.86	9.46
IAA	20.48	17.71	13.40	14.50	12.97	10.97	12.04
B	9.67	8.13	7.86	7.20	7.47	6.22	6.58
T	16.93	13.41	12.62	11.31	11.31	9.76	9.76
EB	22.59	18.18	16.80	16.99	16.20	13.24	14.09
CB	36.03	27.20	25.90	23.11	21.88	17.14	18.41
PB	34.91	27.88	24.53	23.43	22.51	18.44	19.29
IPB	24.14	23.27	17.58	20.14	16.91	16.33	16.33

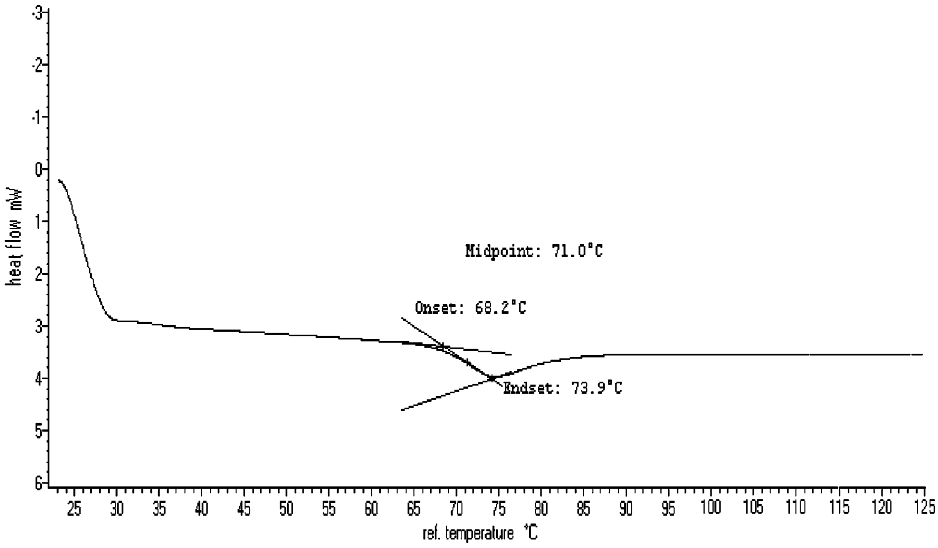


Fig. 3. DSC thermogram of (P*t*BuA-*b*-PMMA).

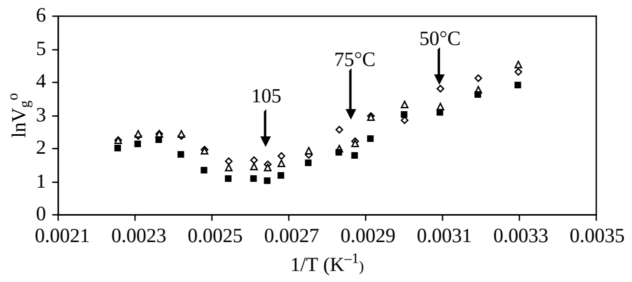


Fig. 4. Retention diagrams of BA (△), IBA (■) and *t*BA (◇) on poly(*t*BuA-*b*-MMA) after thermal process. Arrows indicate T_gs.

macroinitiator for ATRP of MMA using CuCl/PMDETA as the catalyst system in at 80 °C. This produced diblock copolymer (P*t*BuA-*b*-PMMA) with a controlled molecular weight and low polydispersity as given in Table 1.

The GPC traces of macroinitiator and diblock copolymer are portrayed in Fig. 1.

The absence of the P*t*BuA macroinitiator peak on the GPC trace of block copolymer indicates that the macroinitiator was fully converted to the block copolymer. The composition of block copolymer was elucidated by ^{1}H NMR measurements. The ^{1}H NMR spectra of poly(*t*BuA-*b*-MMA) block copolymer exhibit major peaks that are characteristics of the *t*BuA and MMA segments.

The specific retention volumes, V_g^0 of the solvents were obtained experimentally from IGC measurements using Eq. (1). Graphical results were given for BA, IBA and *t*BA between 40 and 170 °C in Fig. 2. Numerical results were given for other acetates and aromatic solvents between 140 and 170 °C in Table 2.

In Fig. 2, the T_gs of poly(*t*BuA-*b*-MMA) block copolymer were determined as 50, 75 and 100 °C from the first deviated point from linearity as the temperature increases. The T_gs of poly(*t*BuA) and poly(MMA) are 50 and 100 °C, respectively. Therefore, 50 and 100 °C should be belonged to the corresponding homopolymer phases. Intermediate one (75 °C) might exhibit the T_g of the joint point phases of two blocks of the copolymers. However, only one T_g at 71 °C could be observed for the poly(*t*BuA-*b*-MMA) block copolymer from DSC measurement as given in Fig. 3.

In order to understand the reason of discrepancy between T_gs, the block copolymer in the column was heated to 170 °C, waited there 10 min and then cooled rapidly to 0 °C by dipping the column into iced water. The retention diagrams of poly(*t*BuA-*b*-MMA) for BA, IBA and *t*BA were obtained over again at temperature range from 40 to 170 °C as seen in Fig. 4.

T_gs at 50 and 75 °C were observed again, however T_g at 100 °C slightly increased to 105 °C. This indicates that a micro phase separation is present at both room temperature and 170 °C in the block copolymer. P*t*BuA and PMMA blocks in the diblock copolymer exhibit their own T_gs at 50 and around 100 °C, in the same time, a region is present between the phases of P*t*BuA and PMMA exhibiting a T_g around 75 °C which is detected by DSC as 71 °C. These results suggest that IGC is more sensitive and reliable than DSC technique to observe micro phase separation of a block copolymer.

The polymer–solvent interaction parameters, χ_{12}^{∞} and χ_{12}^{*} were determined from Eqs. (2) and (3), respectively, between 140 and 170 °C before quenching and between 150 and 170 °C after quenching since thermodynamic equilibrium occurred at this temperature range. The specific volume of the diblock copolymer was calculated by summation of the specific volume of corresponding homopolymers in proportion of their mole fraction [18]. The values of χ_{12}^{∞} and χ_{12}^{*} were given in Tables 3 and 4, respectively. The values of χ_{12}^{∞} greater than 0.5 represent unfavorable polymer–solvent interactions while the values lower than 0.5 indicate favorable interactions in polymer solutions.

In the case of alkyl substituted solvents, the values of χ_{12}^{∞} and χ_{12}^{*} increase with the molecular weight and branching of the substituted aliphatic group of the esters and aromatics except *t*BA. This suggests that the larger sized substituted alkyl groups inhibit the attractive interactions between ester groups of the copolymer and solvents. In the case of CB, electronegative chlorine group on the aromatic ring increases the attractive forces between ester groups of the copolymer and benzene ring. Therefore, CB are better solvent than B, however, T, EB, PB and IPB are becoming poorer with their increasing molecular weight. In the case of acetates, the solvent quality decrease in the following order: *t*BA, EA, PA, IPA, BA,

Table 3
Flory–Huggins polymer–solvent interaction parameters, χ_{12}^{∞} of poly(*t*BuA-*b*-MMA) with the solvents given before (1) and after (2) thermal process

Solvents	140$^{(1)}$	150$^{(1)}$	150$^{(2)}$	160$^{(1)}$	160$^{(2)}$	170$^{(1)}$	170$^{(2)}$
EA	0.62	0.58	0.61	0.50	0.47	0.45	0.51
PA	0.68	0.63	0.70	0.57	0.53	0.49	0.48
IPA	0.70	0.57	0.73	0.63	0.60	0.60	0.49
BA	0.77	0.66	0.88	0.63	0.70	0.54	0.58
IBA	0.78	0.71	0.74	0.57	0.62	0.52	0.53
*t*BA	−0.19	−0.40	−0.20	−0.48	−0.40	−0.40	−0.46
IAA	0.86	0.71	0.99	0.64	0.75	0.67	0.58
B	0.55	0.52	0.55	0.45	0.41	0.41	0.36
T	0.56	0.57	0.63	0.52	0.52	0.46	0.46
EB	0.79	0.75	0.83	0.58	0.63	0.60	0.54
CB	0.39	0.42	0.47	0.35	0.41	0.43	0.36
PB	0.84	0.78	0.91	0.70	0.74	0.69	0.65
IPB	0.97	0.74	1.02	0.63	0.81	0.60	0.60

Table 4
Equation-of-state polymer–solvent interaction parameters, χ^*_{12}, of poly(*t*BuA-*b*-MMA) with the solvents given before (1) and after (2) thermal process

Solvents	$140^{(1)}$	$150^{(1)}$	$150^{(2)}$	$160^{(1)}$	$160^{(2)}$	$170^{(1)}$	$170^{(2)}$
EA	0.88	0.87	0.89	0.80	0.77	0.77	0.83
PA	0.92	0.88	0.96	0.84	0.80	0.78	0.77
IPA	0.96	0.84	1.00	0.92	0.89	0.91	0.80
BA	0.97	0.88	1.10	0.86	0.93	0.78	0.82
IBA	1.00	0.94	0.97	0.82	0.87	0.79	0.80
*t*BA	0.06	−0.13	0.06	−0.20	−0.12	−0.10	−0.17
IAA	1.05	0.91	1.19	0.85	0.96	0.90	0.80
B	0.76	0.74	0.77	0.68	0.65	0.66	0.60
T	0.74	0.75	0.81	0.72	0.72	0.67	0.67
EB	0.94	0.92	0.99	0.75	0.79	0.79	0.72
CB	0.53	0.58	0.58	0.51	0.51	0.60	0.52
PB	0.98	0.94	1.06	0.86	0.90	0.85	0.81
IPB	1.11	0.89	1.17	0.79	0.97	0.77	0.77

IBA and IAA for the poly(*t*BuA-*b*-MMA) at studied temperature range in the same time, solvent quality of aromatics and acetates increase with temperature and they tend to become good solvent at high temperatures, exhibiting endothermic solubility behavior. There is no any information related to the interaction parameters of poly(*t*BuA-*b*-MMA) for comparison in the literature. It is possible to compare the data obtained in this study with the data of poly(methyl methacrylate) since the major component of the poly(*t*BuA-*b*-MMA) is block (methyl methacrylate) (95%). The parameters χ^*_{12} given in Table 4 in the present study are comparable with the parameters of PMMA-ester systems in our earlier study, which are extrapolated to 170 °C from higher temperatures [19]. The parameters χ^∞_{12} of B and T in Table 4 are also comparable with the parameters given in literature as 0.41 and 0.40, respectively [20].

Table 5
The effective exchange energy parameter, X_{eff}, (J/cm^3) of poly(*t*BuA-*b*-MMA) with the solvents given before (1) and after (2) thermal process

Solvents	$140^{(1)}$	$150^{(1)}$	$150^{(2)}$	$160^{(1)}$	$160^{(2)}$	$170^{(1)}$	$170^{(2)}$
EA	12.7	12.2	13.4	9.3	7.7	8.8	12.1
PA	12.3	10.9	14.5	8.6	6.6	6.0	5.6
IPA	12.9	8.7	16.3	12.8	11.1	12.4	7.2
BA	16.4	11.4	20.1	10.6	13.5	7.6	9.1
IBA	12.8	11.1	12.2	6.4	8.1	5.2	5.6
*t*BA	−24.1	−32.8	−24.8	−36.8	−33.5	−32.0	−34.8
IAA	17.5	13.2	23.5	10.8	15.0	11.5	7.9
B	18.5	18.0	20.0	14.1	11.8	13.7	10.2
T	16.4	17.2	20.2	14.6	14.6	12.7	12.7
EB	24.2	22.1	25.5	16.5	18.5	17.1	14.4
CB	11.0	10.4	10.4	8.4	8.4	12.5	8.7
PB	21.7	20.3	25.0	17.5	19.1	17.6	16.1
IPB	26.9	19.1	29.4	15.6	22.2	15.1	15.1

Table 6
The weight fraction activity coefficient of solvents at infinite dilution, Ω_1^∞, of poly(*t*BuA-*b*-MMA) with the solvents given before (1) and after (2) thermal process

Solvents	$140^{(1)}$	$150^{(1)}$	$150^{(2)}$	$160^{(1)}$	$160^{(2)}$	$170^{(1)}$	$170^{(2)}$
EA	7.73	7.63	7.79	7.13	6.93	6.97	7.38
PA	7.98	7.69	8.27	7.34	7.04	6.91	6.85
IPA	8.71	7.74	9.15	8.54	8.13	8.28	7.43
BA	8.73	7.94	9.83	7.78	8.34	7.18	7.44
IBA	9.57	9.04	9.30	8.02	8.40	7.74	7.82
*t*BA	3.46	2.85	3.45	2.65	2.87	2.95	2.76
IAA	9.13	7.98	10.54	7.51	8.40	7.80	7.11
B	7.11	6.98	7.22	6.58	6.34	6.43	6.08
T	7.20	7.29	7.74	7.02	7.02	6.70	6.70
EB	8.91	8.65	9.36	7.35	7.70	7.58	7.12
CB	4.67	4.85	5.10	4.55	4.80	4.95	4.61
PB	9.33	8.92	10.14	8.24	8.58	8.24	7.88
IPB	10.67	8.55	11.31	7.74	9.22	7.60	7.60

Table 7
The partial molar heat of sorption, $\Delta\bar{H}_{1,\text{sorp}}$ (kcal/mol), the partial molar heat of mixing, $\Delta\bar{H}_1^{\infty}$ (kcal/mol), molar heat of vaporization, ΔH_v (kcal/mol) obtained by Eq. (8) and molar heat of vaporization, ΔH_v (kcal/mol) calculated from the relation given in the literature [21] at normal boiling temperature T_b (°C) before (1) and after (2) thermal process

Solvents	$-\Delta\bar{H}_{1,\text{sorp}}{}^{(1)}$	$-\Delta\bar{H}_{1,\text{sorp}}{}^{(2)}$	$\Delta\bar{H}_1^{\infty(1)}$	$\Delta\bar{H}_1^{\infty(2)}$	$\Delta H_v^{(1)}$	$\Delta H_v^{(2)}$	$\Delta H_v^{(\text{lit})}$	T_b (°C)
EA	5.2	5.5	1.4	1.0	6.6	6.5	7.7	77.3
PA	5.8	3.9	1.7	3.5	7.5	7.4	8.2	101.8
IPA	6.7	3.0	0.3	3.9	7.0	6.9	7.8	89
BA	6.2	3.9	2.2	4.5	8.4	8.4	9.0	126.2
IBA	5.2	3.9	2.7	4.1	7.9	8.0	8.6	117
*t*BA	7.8	3.4	2.0	6.4	9.8	9.8	8.0	97
IAA	7.5	1.9	1.9	7.3	9.4	9.3	9.0	139
B	5.3	3.2	1.3	3.3	6.6	6.5	7.3	80.3
T	6.6	4.8	0.9	2.7	7.5	7.5	7.9	110.8
EB	6.1	5.1	2.4	3.3	8.5	8.4	8.5	136.3
CB	8.7	6.4	−0.4	1.9	8.3	8.3	8.7	131.9
PB	7.6	4.5	1.6	4.7	9.2	9.2	9.1	159.4
IPB	4.7	1.4	4.1	7.4	8.8	8.8	9.0	152.6

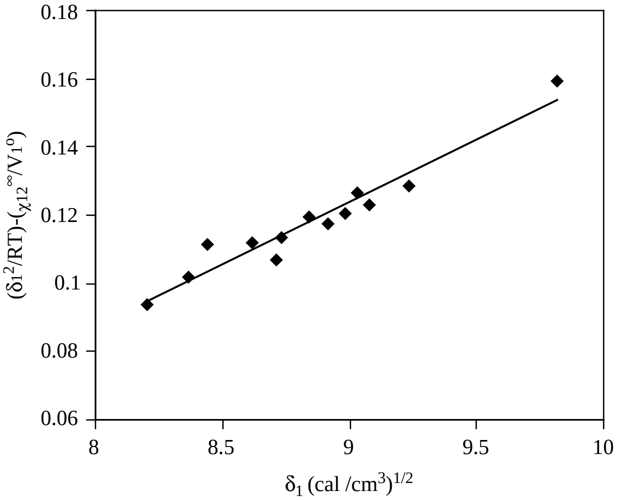


Fig. 5. Variation of the term $[(\delta_1^2/RT)-(\chi_{12}^{\infty}/V_1^0)]$ with solubility parameters of the solvents, δ_1 (cal/cm^3)$^{1/2}$ before thermal process at 25 °C.

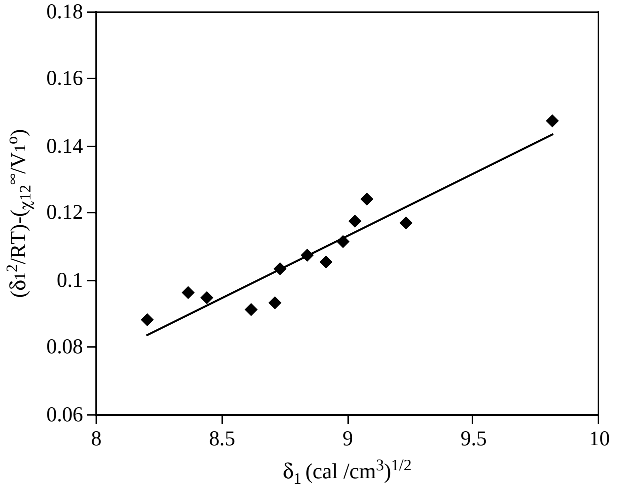


Fig. 6. Variation of the term $[(\delta_1^2/RT)-(\chi_{12}^{\infty}/V_1^0)]$ with solubility parameters of the solvents, δ_1 (cal/cm^3)$^{1/2}$ after thermal process at 25 °C.

The effective exchange energy parameters, X_{eff} in the equation-of-state theory were obtained from Eq. (5) and results were given in Table 5.

It was determined that X_{eff} of poly(*t*BuA-*b*-MMA) with EA, PA, IPA, BA, IBA, IAA, B, T, EB, PB and IPB fairly decreased with temperature. This indicates that exchanging a polymer segment in the bulk state with a solvent molecule becomes easier as temperature increases.

$\Delta\bar{H}_{1,\text{sorp}}$ and $\Delta\bar{H}_1^{\infty}$ were obtained from the slopes of the plots of ln V_g^0 versus $1/T$ and ln Ω_1^{∞} versus $1/T$ by means of Eqs. (5) and (6), respectively, at temperature range of 140–170 °C before thermal process and at temperature range of 150 and 170 °C after thermal process. The weight fraction activity coefficient of solvents at infinite dilution, Ω_1^{∞} was obtained from Eq. (7) and given in Table 6.

In Table 7, the values of ΔH_v obtained from Eq. (8) were compared to the values of ΔH_v calculated according to the Ref. [21]. The agreement is good for the solvents that boiling temperature is close to the average of the studied column temperature.

The solubility parameter of poly(*t*BuA-*b*-MMA), δ_2 was determined from the slope and intercept of the plots drawn according to Eq. (9). Sinceχ_{12}^{∞} varies linearly with $1/T$, χ_{12}^{∞} values at studied temperatures can be extrapolated to 25 °C [22]. By means of Eq. (9), δ_2 was determined as 10.9 and 11.1 (cal/cm^3)$^{1/2}$ by using the values of χ_{12}^{∞} at 25 °C both before and after thermal process in Figs. 5 and 6, respectively.

4. Conclusions

It was observed by IGC technique that poly(*t*BuA-*b*-MMA) diblok copolymer with a short *t*BuA segment exhibits three T_gs which do not disappear by quenching. It was concluded that the copolymer underwent microphase separation. It seems that IGC technique can detect the T_g of the phases with small sized domain since T_g of the short P*t*BuA block of the diblock copolymer can be observed by IGC in the contrary of DSC. The solvent quality decrease with the molecular weight and branching of the substituted aliphatic group of the esters and aromatics except *t*BA at studied temperature range before and after quenching. This suggests that the larger sized substituted alkyl groups inhibit the favorable interactions between ester groups of the copolymer and solvents. Chlorine substitution increases the solubility of copolymer because of dipole–dipole interaction. The solubility parameter of poly(*t*BuA-*b*-MMA) diblok copolymer, δ_2 is found to be 11.0 $(\mathrm{cal/cm^3})^{1/2}$ at 25 °C.

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