



Ultrasonic degradation of poly (styrene-co-alkyl methacrylate) copolymers

Sasikiran Pasupuleti, Giridhar Madras *

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

ARTICLE INFO

Article history:

Received 23 September 2009

Accepted 5 February 2010

Available online 11 February 2010

Keywords:

Ultrasonic degradation

Styrene-co-alkyl methacrylates

Copolymers

Rate coefficients

Thermal stability

ABSTRACT

The ultrasonic degradation of poly (styrene-co-methyl methacrylate) (SMMA), poly (styrene-co-ethyl methacrylate) (SEMA) and poly (styrene-co-butyl methacrylate) (SBMA) copolymers of different compositions was studied. The copolymers were synthesized and NMR spectroscopy was used to determine the composition, and the glass transition temperatures were determined by DSC. The reactivity ratios were determined by the Kelen–Tudos method and it indicated that the copolymers were random. The effect of solvent, temperature and copolymer composition on the ultrasonic degradation rate of these copolymers was investigated. A model based on continuous distribution kinetics was employed to study the degradation kinetics. The degradation rate coefficients of the copolymers decreased with an increase in the styrene content in the copolymer. At any particular copolymer composition the rate of degradation follows the order: SBMA > SEMA > SMMA. Thermogravimetric analysis (TGA) of the copolymers was carried in order to assess their thermal stability. The same order of degradation was observed for the thermal degradation of the copolymers as that observed for ultrasonic degradation.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The copolymers of styrene and alkyl methacrylates represent a widely-used class of copolymers since they exhibit great diversity of properties compared to those of homopolymers [1]. Their high thermal and chemical stability, high transparency, easy formability, good electrical and mechanical properties [2] has led them to be used for a variety of applications in medicine, paper and paint industry, textiles and automobiles etc. For example, solid polystyrene is used in disposable cutlery, plastic models, CD and DVD cases, and the expanded form of polystyrene is used for packing materials and insulation [3]. Poly(alkyl methacrylates) are mainly used in intraocular lenses, control drug delivery systems and adhesives, respectively. The copolymers of styrene and alkyl methacrylates are used in gamma irradiation shields, plastic optical fibers and synthetic resins [3].

The common method of degradation is by the use of thermal or chemical energy. Among the alternative methods of polymer degradation, ultrasonic degradation is interesting because unlike chemical and thermal degradation methods, ultrasonic degradation occurs by non-random mid point scission [4]. The overall degradation mechanism of polymer molecules in presence of ultrasound is primarily by the action of intense shear fields set up by the collapsing cavities of microbubbles [5]. The influence of various factors such as solvent, temperature, ultrasound intensity [6], polymer concentration [4], initial molecular weight [7],

dissolved gases [8], viscosity and surface tension [9,10] affecting the degradation of different polymer solution systems has been investigated in various studies.

Many theoretical [11–13] and phenomenological models [14–16] have been proposed by several researchers to evaluate the kinetics of the ultrasonic degradation process. All of these models offer the same rough description of the reduction of the average molecular weight during the process [17]. All the models show that the polymer degrades rapidly in the initial phase of the process, and then the rate of decrease of molecular weight slows down and approaches a limiting molecular weight. Continuous distribution kinetic models [7,9,18] have been successfully used to determine the degradation rate coefficient and the same approach has been followed in this study.

The ultrasonic degradation of polystyrene [8,19], poly(methyl methacrylate) [20], poly(vinyl-pyrrolidone) [21], poly(ethylene oxide) [22,23], poly(vinyl acetate) [4,24], poly(vinyl alcohol) [25], poly(alkyl methacrylates) [26] has been studied. The ultrasonic degradation of poly(methyl methacrylates-co-alkyl acrylate) copolymers was investigated [27] and it was shown that the degradation rate varies linearly with the alkyl acrylate content in the copolymer. However, ultrasonic degradation of copolymers and the effect of copolymer composition on the degradation rate have not been well studied.

In this work, poly (styrene-co-alkyl methacrylates) copolymers, viz. poly (styrene-co-methyl methacrylate) (SMMA), poly (styrene-co-ethyl methacrylate) (SEMA) and poly (styrene-co-butyl methacrylate) (SBMA) over the entire range of composition were prepared and the kinetics of the ultrasonic degradation was studied. To the

* Corresponding author. Tel.: +91 80 2293 2321; fax: +91 80 2360 0683.

E-mail address: giridhar@chemeng.iisc.ernet.in (G. Madras).

best of our knowledge, this is the first study on the ultrasonic degradation of poly (styrene-co-alkyl methacrylate) copolymers. The main objective of our study was to investigate the effect of copolymer composition and alkyl group substituent on the ultrasonic degradation and compare the trend with the thermal stability of these copolymers.

2. Experimental

2.1. Materials and methods

The monomers, styrene, methyl methacrylate, ethyl methacrylate and butyl methacrylate were procured from Sigma–Aldrich (USA) and washed with 5% caustic solution in order to remove inhibitors. This was followed by distillation under pressure to ensure the purity of monomers. The solvents, benzene, chlorobenzene, *o*-dichlorobenzene, toluene, and *p*-xylene; and the initiator, azo-bis-isobutyronitrile (AIBN) were purchased from S.D. fine chemicals (India). The solvents were distilled and filtered through 0.2 μm nylon filter paper before use.

2.2. Polymerization

All polymers were synthesized by using conventional free radical polymerization technique using AIBN (5% wt.) as the initiator at 60 °C. The synthesized polymers were fractionated by dissolving in toluene and subsequent precipitation in methanol.

2.3. Ultrasonic degradation experiments

Polymer solutions of 2 g/L were prepared and 60 mL of the polymer solution was subjected to ultrasonic degradation using a horn-type ultrasonic processor (Vibronics, India) with an intensity of 36 W/cm². SMMA-54 (styrene–methyl methacrylate copolymer with 54 mol% of methyl methacrylate) was degraded in different solvents at 30 °C to understand the effect of solvents and was also degraded at different temperatures from 30 to 60 °C in *o*-dichlorobenzene. The temperature of the solution was maintained constant (± 2 °C) using a thermostatic water bath. The homopolymers and copolymers of different compositions were degraded in *o*-dichlorobenzene at 30 °C. Further details of the experimental setup can be found elsewhere [27]. Samples of 200 μL were collected for further analysis by gel permeation chromatography (GPC). To obtain the limiting molecular weight of the polymers, experiments were carried for 10 h and no significant change was observed in molecular weight after 8 h. Several experiments were repeated in triplicate and the error in estimation of rate coefficient was less than 4%.

2.4. GPC analysis

The molecular weight (MW) distributions of the samples were determined by GPC that consisted of a high pressure liquid chromatography (HPLC) pump, three size exclusion columns packed with cross linked poly (styrene-divinyl benzene) (Styragel HR 5E, HR 4, HR 1) [300 mm \times 7.5 mm], a differential refractometer

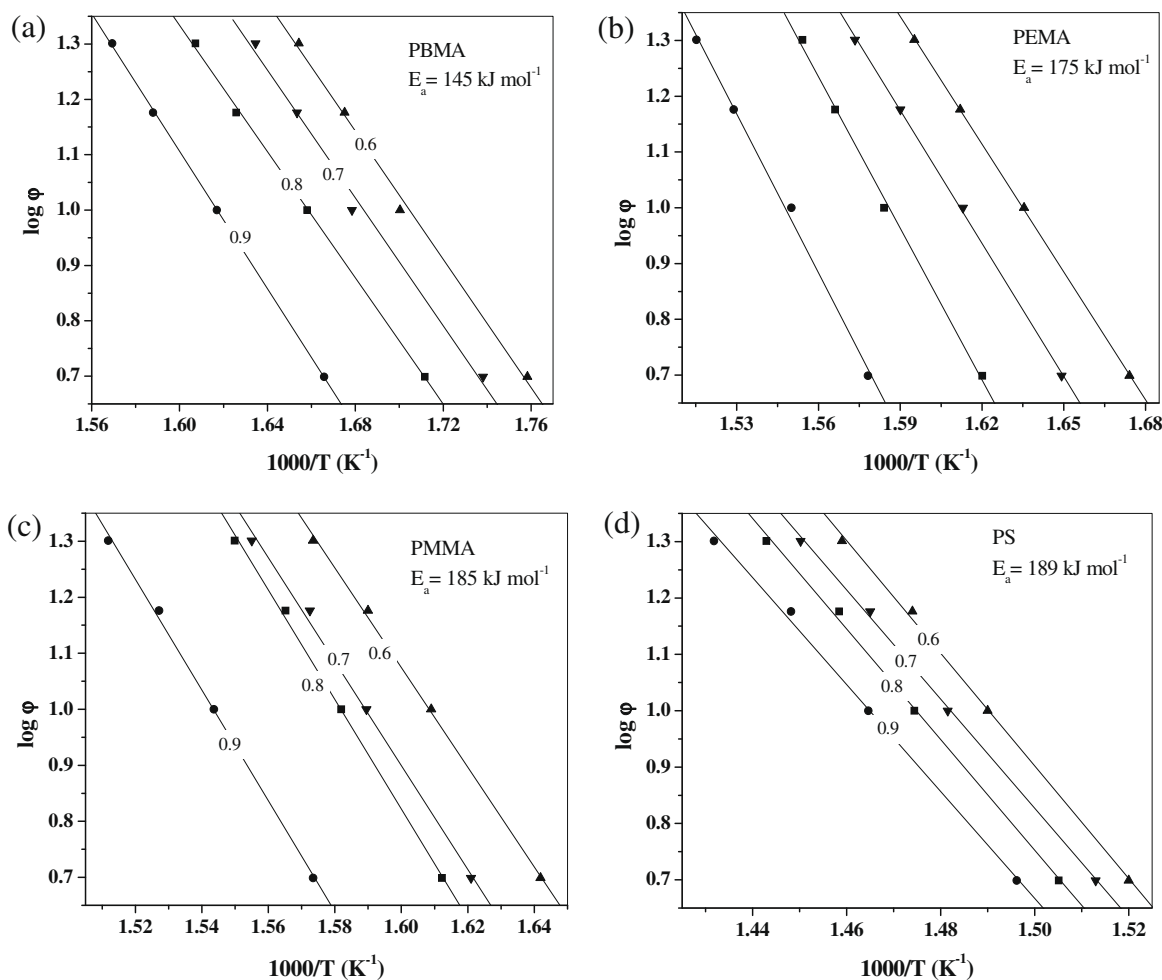


Fig. 1. Ozawa plots to determine activation energies of homo polymers (a) PBMA, (b) PEMA, (c) PMMA and (d) PS. The numbers on the plot indicate conversion.

(Waters RI 2410) for detection, and a data acquisition system to store the data. The samples were injected through a Rheodyne 7725i valve with a sample loop of 50 μL . The obtained chromatogram was converted to molecular weight distribution (MWD) using universal calibration [28]. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min.

2.5. NMR characterization

^1H NMR (400 MHz, Bruker) spectroscopy was used to determine the compositions of the synthesized copolymers, using CDCl_3 as solvent and tetramethylsilane (TMS) as reference.

2.6. TGA analysis

All the homo polymers and copolymers (10–15 mg) were subjected to pyrolysis using the Perkin–Elmer Pyris-Diamond thermogravimetric-differential thermal analyzer (TG/DTA) in an inert atmosphere (nitrogen flow at 150 cm^3/min) at different heating rates (5–20 $^\circ\text{C}/\text{min}$) in the temperature range of 30–700 $^\circ\text{C}$.

2.7. DSC analysis

The calorimetric (DSC) measurements were carried out on a DSC823^e differential scanning calorimeter (Mettler Toledo, US)

operating in a nitrogen atmosphere. The sample size was around 20 mg. The analysis was performed at the heating rate of 5 $^\circ\text{C}/\text{min}$.

3. Theoretical model

Continuous distribution kinetics was used in this study to determine the degradation rate coefficients [27]. For a polymer $P(x)$, the ultrasonic midpoint degradation can be represented as follows [28]

$$P(x) \xrightarrow{k(x)} 2P(x/2) \quad (1)$$

The population balance equation for the above equation can be written as [7]

$$\frac{\partial p(x, t)}{\partial t} = -\kappa(x)p(x, t) + 2 \int_x^\infty \kappa(x')p(x', t)\delta\left(x - \frac{x'}{2}\right)dx' \quad (2)$$

The degradation rate coefficient is assumed to be of the form $\kappa(x) = k(x - x_i)$, where x_i is the limiting molecular weight [23]. This form of the rate equation indicates that no further degradation is possible after the polymer reaches its limiting molecular weight. Applying the moment operation and solving the moment equations yields the variation of the number average molecular weight (M_n) as [27]

$$\ln\left(\frac{\frac{1}{M_{n0}} - \frac{1}{x_i}}{\frac{1}{M_n} - \frac{1}{x_i}}\right) = \ln(Y) = kx_i t \quad (3)$$

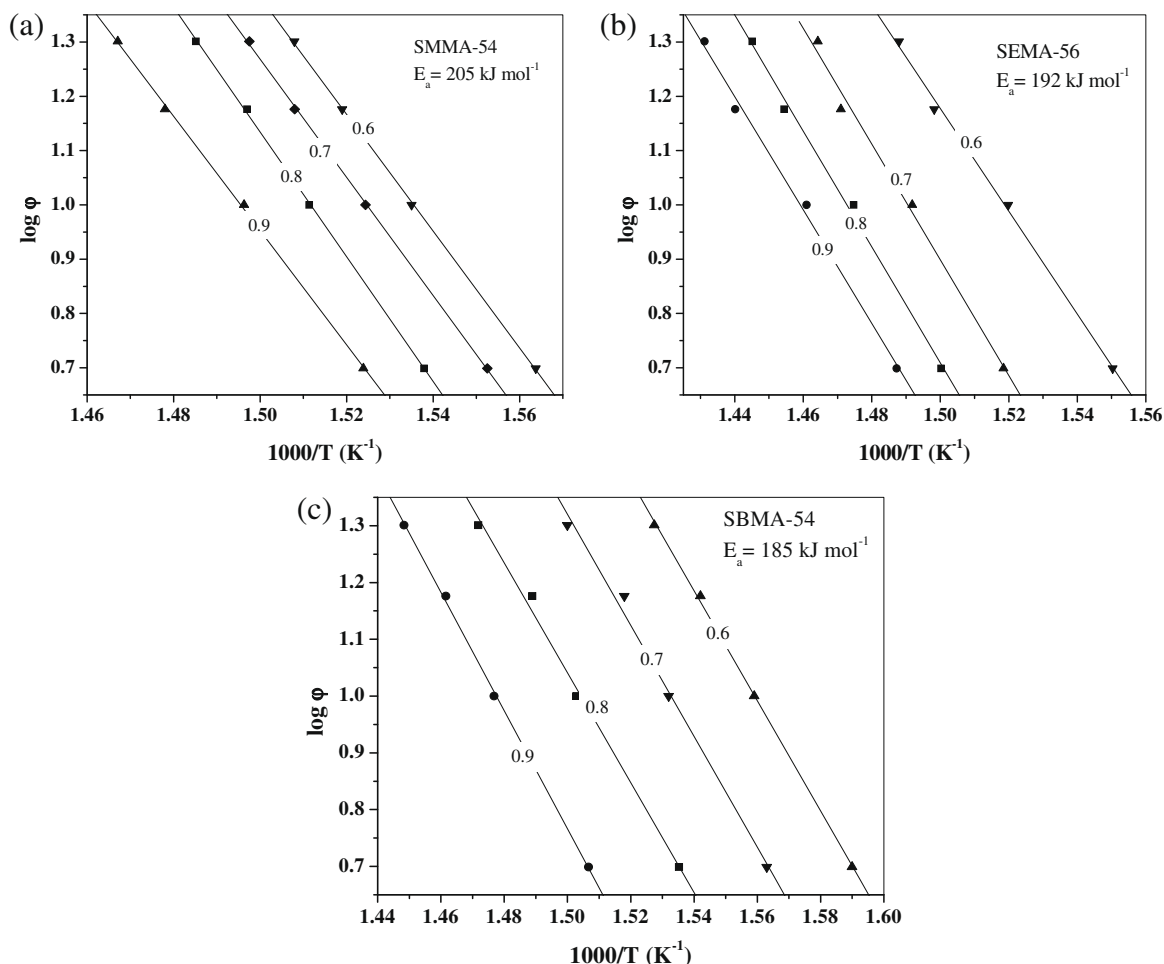


Fig. 2. Ozawa plots to determine activation energies of (a) SMMA-54, (b) SEMA-56 and (c) PBMA-54 copolymers.

4. Results and discussion

4.1. Copolymer composition

All copolymers were analyzed using 400 MHz ^1H NMR spectroscopy, and the compositions of the copolymers were calculated by identifying and quantifying the signal peaks of the monomers. The ^1H NMR spectrum of SMMA-54 (54 mol% methyl methacrylate) copolymer is shown in Fig. S1 (see supplementary information). It is reported that styrene shows a peak at $\delta = 7.1$ [29,30] and MMA at $\delta = 2.8$ – 3.6 [30,31] corresponding to the phenyl ring ($-\text{C}_6\text{H}_5$) and the methoxy ester linkage ($-\text{COOCH}_3$), respectively. These peaks were identified in all copolymers and compositions of the copolymers were calculated from the integral peak areas [29,31]. Similarly the compositions of SEMA and SBMA copolymers were computed from integrating the signal peak areas of EMA at $\delta = 3.8$ [32,33] and of BMA at $\delta = 4.2$ [32–34].

The Kelen–Tudos method [35] was used to calculate the reactivity ratios of monomers in copolymers and the equation for this method can be written as

$$\frac{x(y-1)}{\alpha y + x^2} = \frac{(r_1 + r_2/\alpha)x^2}{\alpha y + x^2} - \frac{r_2}{\alpha} \quad (4)$$

where x and y are the molar ratios of monomers in feed and copolymer, respectively. The parameter, $\alpha = \sqrt{\frac{x_{\min}x_{\max}}{y_{\min}y_{\max}}}$, where x_{\min} , x_{\max} are minimal and maximal molar ratios of monomers in feed; y_{\min} , y_{\max} are minimal and maximal molar ratios of monomers in the copolymers. Using $\eta = \frac{x(y-1)}{\alpha y + x^2}$ and $\xi = \frac{x^2}{\alpha y + x^2}$ Eq. (4) can be written as

$$\eta = (r_1 + r_2/\alpha)\xi - \frac{r_2}{\alpha} \quad (5)$$

Thus the reactivity ratios r_1 and r_2 can be determined from the slope and intercepts of the plot of η against ξ . The Kelen–Tudos plots for SMMA, SEMA and SBMA are shown in Fig. S2 (see supplementary information). The monomer reactivity ratios for the copolymer SMMA are $r_1(\text{S}) = 0.57$ and $r_2(\text{MMA}) = 0.54$, for the copolymer SEMA are $r_1(\text{S}) = 0.65$ and $r_2(\text{EMA}) = 0.32$ and for the copolymer SBMA are $r_1(\text{S}) = 0.52$ and $r_2(\text{BMA}) = 0.46$, and the values are comparable with the values reported in literature [36]. The product of reactive ratios for each copolymer is lower than unity, indicating that all copolymers are random copolymers.

4.2. Thermal degradation

Thermal degradation of the copolymers and homopolymers was studied using thermogravimetry at different heating rates of 5, 10, 15 and 20 $^\circ\text{C}$ were used. The activation energies of the polymers at different conversions (α) were calculated by using the Ozawa method [37]. In this method, the variation of conversion (α) with heating rate is given by

$$\log\left(\int_0^\alpha \frac{d\alpha}{g(\alpha)}\right) = \log\left(\frac{AE}{R}\right) - \log \varphi - 2.315 - 0.4567\left(\frac{E}{RT}\right) \quad (6)$$

At fixed conversion, the activation energies are obtained from the slope of the plot of $\log \varphi$ against $1/T$.

The Ozawa plots of homopolymers (PS, PMMA, PEMA and PBMA) and copolymers (SMMA-54, SEMA-56 and SBMA-54) are shown in Figs. 1 and 2, respectively. The normalized weight loss profiles of SMMA, SEMA and SBMA copolymers of different compositions are shown in Fig. S2 (see supplementary information). It can be inferred that the thermal stability of copolymers is higher than that of homopolymers (see Table S1 for activation energies). Fig. 2 depicts the effect of alkyl group substituent on the thermal stability of copolymers, and it follows the order SMMA > SEMA > SBMA.

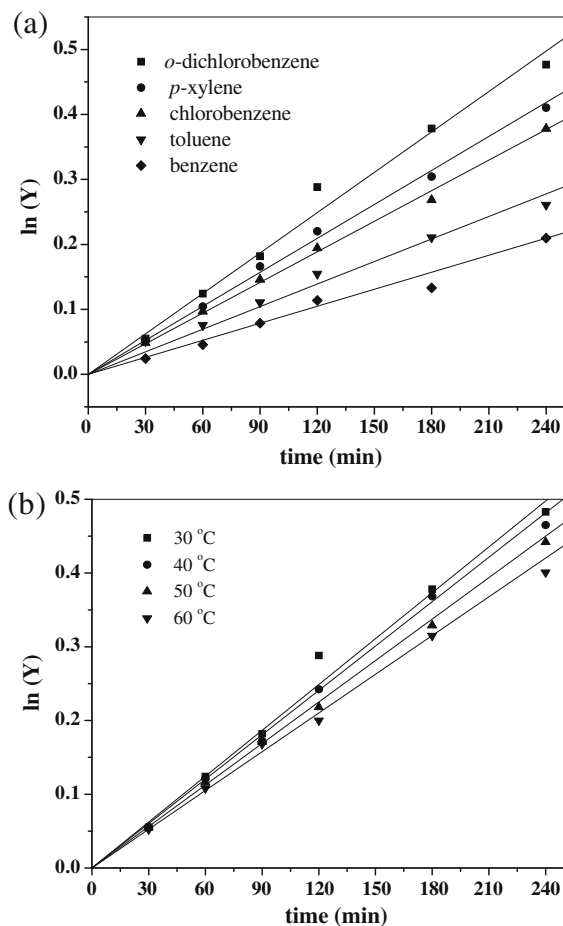


Fig. 3. Variation of $\ln(Y)$ with sonication time for SMMA-54 (a) at 30 $^\circ\text{C}$ in different solvents and (b) in *o*-dichlorobenzene at different temperatures. Solid lines represent model fit.

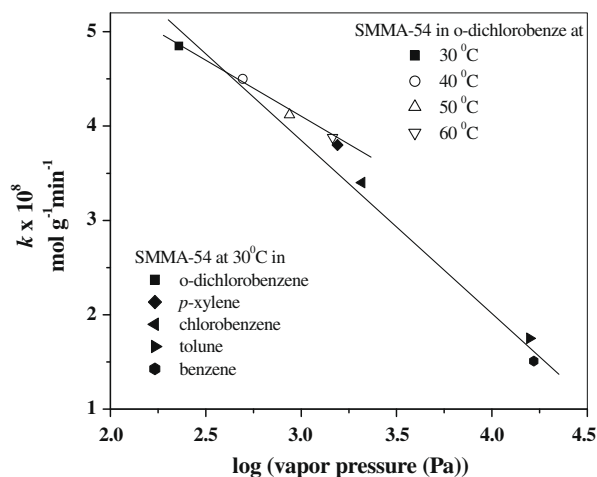


Fig. 4. Variation of degradation rate coefficient of SMMA-54 with vapor pressure of the solvent.

4.3. Differential scanning calorimetry analysis

The glass transition temperatures of the copolymers were determined by using a DSC823^e differential scanning calorimeter and the values are listed in Table S1 (see supplementary information).

It can be observed that the presence of styrene influenced the T_g of SEMA and SBMA copolymers and the effect was low for SMMA copolymers because the glass transition temperatures of their homo polymers are similar. The presence of styrene in

the copolymer increased the T_g of SEMA and SBMA copolymers because of increased chain stiffness [38], and T_g of SMMA decreased due to decreased polar–polar intermolecular interactions between ester groups [39].

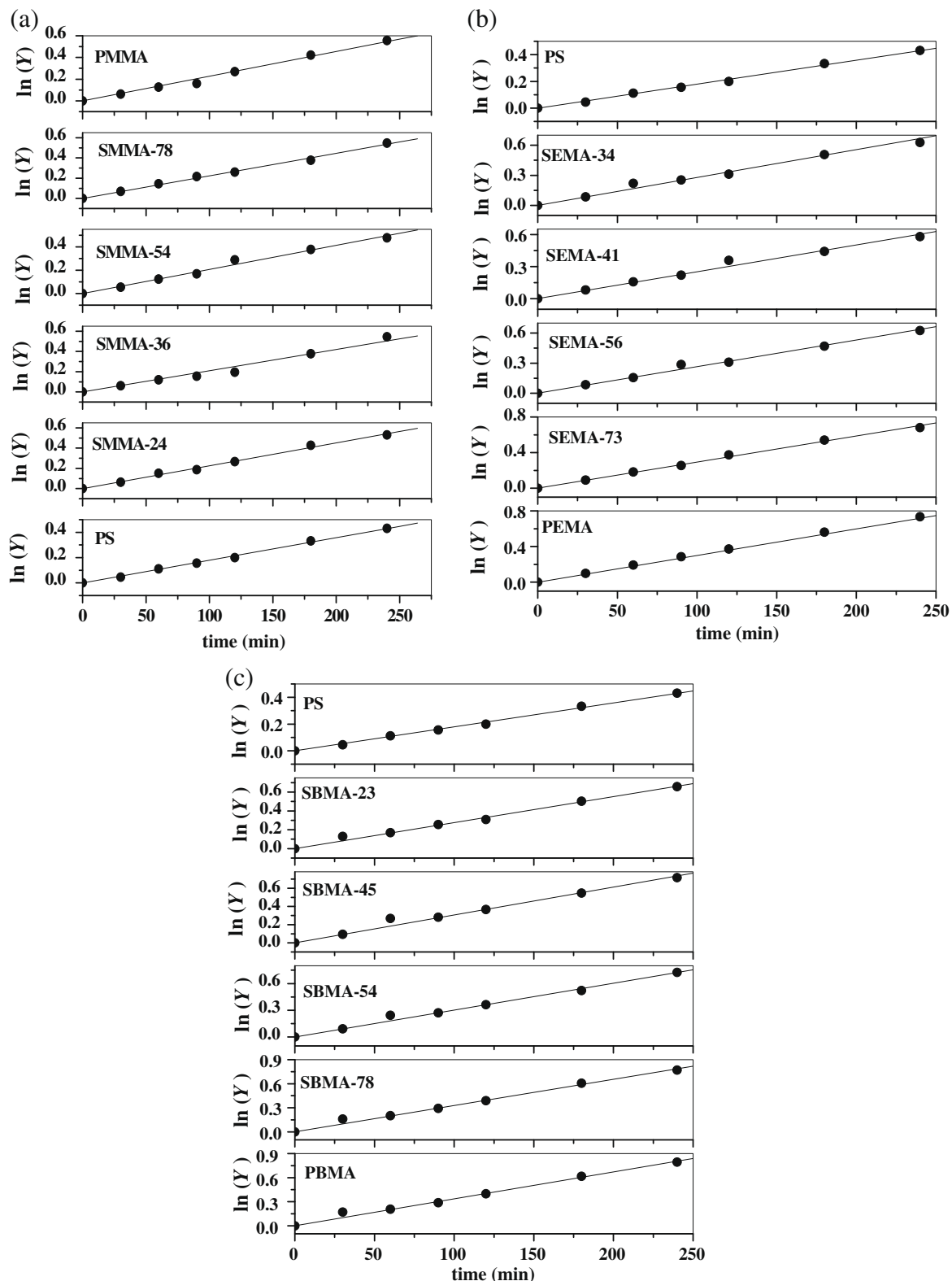


Fig. 5. Variation of $\ln(Y)$ with sonication time of (a) SMMA, (b) SEMA and (c) SBMA copolymers of different composition in *o*-dichlorobenzene at 30 °C. Solid lines represent model fit.

4.4. Ultrasonic degradation

4.4.1. Effect of solvents

The effect of solvents on the ultrasonic degradation of poly (styrene-co-alkyl methacrylate) copolymers was studied by investigating the degradation of SMMA-54 (54 mol% of MMA) at 30 °C using different solvents. Fig. 3a depicts the variation of $\ln(Y)$ with sonication time. The degradation rate coefficient in a particular solvent mainly depends upon the properties of solvent like vapor pressure and kinematic viscosity [5,7,9] which primarily affect the cavitation capacity [40] of the solvent. It was observed that the k value is a maximum in *o*-dichlorobenzene and minimum in benzene. The variation in rate coefficient for different solvents is mainly attributed to their cavitation capacity [10,40] which governs the intensity of shock waves radiated from the collapsing cavity.

4.4.2. Effect of temperature

The effect of temperature on degradation rate coefficient was studied on SMMA-54 copolymer in *o*-dichlorobenzene; the variation of $\ln(Y)$ with sonication time at different temperatures is illustrated in Fig. 3b. It can be observed that the rate coefficient is higher at low temperature and decreases at higher temperature. At higher temperature, clearly the vapor pressure will be higher and so the vapor will enter the cavitation bubble, which leads to the cushioning effect [8,41]. The cushioning effect reduces the shock wave intensity and thus the rate of degradation. The increased viscosity of the solvent at lower temperatures increases rapid transmission of shock waves and favors the defragmentation of polymer chain at low strain rates [8,42]. Fig. 4 shows the effect of solvent vapor pressure on the degradation rate coefficient. The vapor pressure data was taken from standard handbook [43].

4.4.3. Effect of alkyl group substituents

Fig. 5 depicts the variation of $\ln(Y)$ with sonication time for various copolymers of different compositions in *o*-dichlorobenzene at 30 °C. The degradation rate coefficients ($k \times 10^{-8}$) ($\text{mol g}^{-1} \text{min}^{-1}$), obtained from the slope of the figures, of the homo polymers MMA, EMA and BMA are 5.8, 6.4 and 7.4, respectively, while that of copolymers SMMA-54, SEMA-56 and SBMA-54 are 5.0, 5.2 and 5.6, respectively. Fig. 6 shows that at any particular alkyl methacrylate composition, the ultrasonic degradation rate follows the order: SBMA > SEMA > SMMA. It indicates that the degradation rate increases with increase in the chain length of the alkyl methacrylate, which can be attributed to increased chain mobility. The increase of side chain in the polymer enhances the mobility and

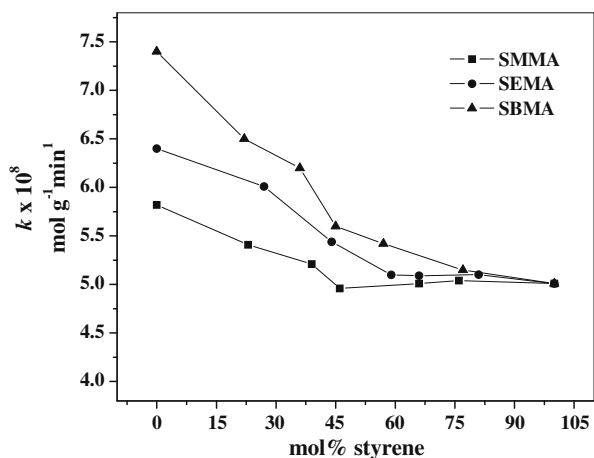


Fig. 6. Variation of degradation rate coefficients of poly (styrene-co-alkyl methacrylate) copolymers with mol% styrene in *o*-dichlorobenzene at 30 °C.

further leads to increased scission in the main chain. A similar trend was observed in the thermal degradation of these copolymers (Fig. 2), as discussed earlier.

4.4.4. Effect of copolymer composition

The dependence of the degradation rate coefficient on copolymer composition of poly (styrene-co-alkyl methacrylate) copolymers was investigated by conducting experiments over the entire range of composition for all copolymers at 30 °C in *o*-dichlorobenzene. The variation of $\ln(Y)$ with sonication time for different composition of SMMA, SEMA and SBMA copolymers is shown in Fig. 5a–c, respectively. It is clear that the model gives good fit to the experimental results. The rate coefficient for the ultrasonic degradation of the homopolymers and the copolymers are determined from the slope of the linearly regressed lines of Fig. 5.

Fig. 6 shows the variation of the rate coefficients with the copolymer composition for various copolymers. It can be observed that an increase in the styrene content in the copolymer has reduced the degradation coefficient of copolymers. This can be ascribed to increased mechanical properties of copolymers. Incorporation of vinyl aromatic monomer such as styrene in copolymer serves to improve the stability (mechanical and thermal) of polymer chains [44]. Further, the degradation rate coefficient is lower for some copolymers than either of the homopolymers, which indicates that the rate of degradation is not linear with styrene content. Similar trends were reported for mechanical properties of styrene alkyl methacrylate copolymers [45–47]. The mechanical properties of copolymers are primarily affected by the arrangement of two monomer units in the polymer backbone which influences the strength of polar–polar intermolecular interactions between monomers [48]. Fig. 7 represents the dependence of ultrasonic degradation coefficient, thermal activation energy, and tensile strength [46] on mol% styrene in the SBMA copolymer.

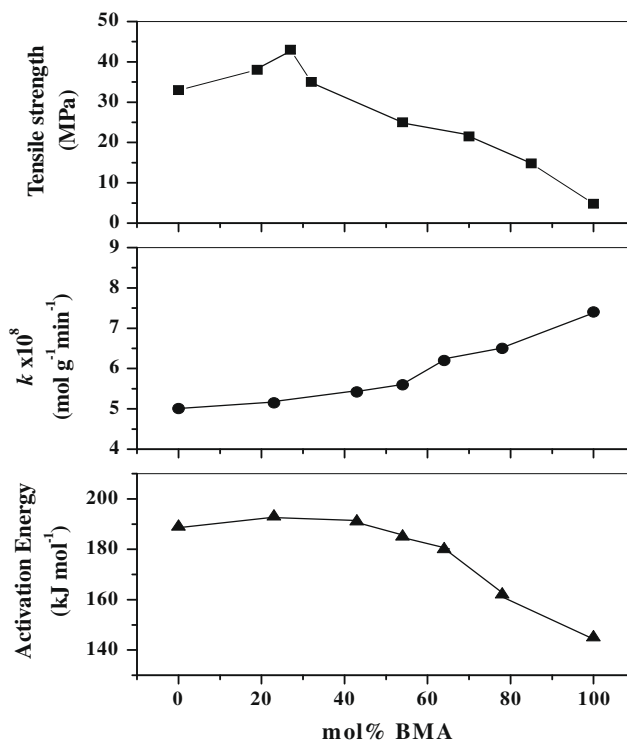


Fig. 7. Variation of thermal activation energy, ultrasonic degradation rate coefficient and tensile strength of poly (styrene-co-butyl methacrylate) copolymers with mol% of BMA.

4.5. Comparison of ultrasonic and thermal degradation

Previous studies have shown that the order of ultrasonic degradation of homopolymers of the alkyl acrylate series [27] follows the order, PBA < PEA < PMA i.e., the rate of degradation of poly (butyl acrylate) is slower than that of poly(methyl acrylate). This indicates that the degradation decreases with an increase in chain length of the side chain. However, the order of degradation of homopolymers of the alkyl methacrylate series [26] follows PBMA > PEMA > PMMA i.e., the degradation of poly(methyl methacrylate) is slower than that of poly(butyl methacrylate). This indicates that the degradation increases with an increase in chain length of side chains. Though the orders for the acrylates and methacrylates seem to be anomalous, the orders are the same as that of thermal degradation of these polymers. Similarly, in this study, similar trends were observed in ultrasonic and thermal degradation of SMMA, SEMA and SBMA copolymers. Though the thermal degradation and mechanical properties of the copolymer are for the polymers in the solid state, the degradation rates of the copolymers in solution under ultrasonic exposure follow the same order (Fig. 7). This study seems to indicate that the degradation rate of the copolymers in solution under ultrasound follows the same order as that of the mechanical strength of the polymers because ultrasonic degradation is similar to degradation under mechanical forces.

5. Conclusions

In the present work the ultrasonic degradation of three different poly (styrene-co-alkyl methacrylate) copolymers, viz. SMMA, SEMA and SBMA over entire range of composition was investigated. The reactivity ratios of the monomers were determined. A model based on continuous distribution kinetics was employed to obtain the degradation rate coefficients. The effect of solvent and temperature on the ultrasonic degradation of styrene–methyl methacrylate copolymer was studied and it is mainly attributed to vapor pressure of the solvent. The presence of styrene in the copolymers decreased the degradation rate coefficient of alkyl methacrylate copolymers mainly because of their improved mechanical properties. For any particular copolymer composition, the ultrasonic degradation rate follows the order SBMA > SEMA > SMMA, and is attributed to increased main chain mobility which increases with the length of side chain. The thermal degradation of the copolymers was also investigated and the same degradation order as that of ultrasonic degradation was observed.

Acknowledgments

The corresponding author thanks the department of science and technology, India for financial support and the Swarnajayanthi fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ultsonch.2010.02.003.

References

- [1] D. Li, N. Li, R.A. Hutchinson, High temperature free radical copolymerization of styrene and butyl methacrylate with depropagation and penultimate kinetic effects, *Macromolecules* 39 (2006) 4366–4373.
- [2] E. Penzel, *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, New York, 1992.
- [3] H.F. Mark, N.M. Bikales, Ch.G. Overberger, G. Menges, J.I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering*, Wiley-Interscience, New York, 1985.
- [4] M.T. Taghizadeh, A. Mehrdad, Ultrasonic degradation of solutions of poly(vinyl acetate) in dioxan: the effects of the temperature and polymer concentration, *J. Polym. Sci. Part B* 42 (2004) 445–451.
- [5] G.J. Price, P.F. Smith, Ultrasonic degradation of polymer solutions-III. The effect of changing solvent and solution concentrations, *Eur. Polym. J.* 29 (1993) 419–424.
- [6] G.J. Price, A.J. White, A.A. Clifton, The effect of high-intensity ultrasound on solid polymers, *Polymer* 36 (1995) 4919–4925.
- [7] S.P. Vijayalakshmi, G. Madras, Effect of initial molecular weight and solvents on the ultrasonic degradation of poly(ethylene oxide), *Polym. Degrad. Stab.* 90 (2005) 116–122.
- [8] G.J. Price, P.F. Smith, Ultrasonic degradation of polymer solutions: 2. The effect of temperature, ultrasound intensity and dissolved gasses on polystyrene in toluene, *Polymer* 34 (1993) 4111–4117.
- [9] G. Madras, S. Kumar, S. Chattopadhyay, Effect of solvent on the ultrasonic degradation of poly (vinyl acetate), *Polym. Degrad. Stab.* 71 (2001) 273–278.
- [10] A.M. Basedow, K.H. Ebert, Ultrasonic degradation of polymers in solutions, *Adv. Polym. Sci.* 22 (1977) 83–148.
- [11] G. Schmid, O.Z. Rommel, The disintegration of macromolecules by ultrasonic waves, *Phys. Chem.* 1851 (939) 659–661.
- [12] Y. Shen, K. Chen, Q. Wang, H. Li, H. Xu, X. Xu, Ultrasonic degradation and copolymerization of poly (vinyl alcohol) with acrylonitrile, *J. Macromol. Sci. Part A* 23 (1986) 1415–1431.
- [13] D.W. Ovenall, G.W. Hastings, P.E. Allen, The degradation of polymer molecules in solution under the influence of ultrasonic waves. Part I. Kinetic analysis, *J. Polym. Sci.* 33 (1958) 207–212.
- [14] F. Rodriguez, C.C. Winding, Mechanical degradation of polyisobutylene solutions, *Ind. Eng. Chem.* 51 (1959) 1281–1287.
- [15] A.T. Giz, H. Catalgil-Giz, M. Sunar, A new model for the evolution of the molecular weight distribution of polymers during ultrasonic chain scission, *Macromol. Theory Simul.* 10 (2001) 117–122.
- [16] N. Xiuyuan, H. Yuefang, L. Bailin, X. Xi, Mechanical degradation and mechanochemical copolymerization of hydroxyethyl cellulose, *Eur. Polym. J.* 37 (2001) 201–206.
- [17] A. Akyüz, H. Catalgil-Giz, A.T. Giz, Kinetics of ultrasonic polymer degradation: comparison of theoretical models with on-line data, *Macromol. Chem. Phys.* 209 (2008) 801–809.
- [18] G. Madras, B.J. McCoy, Molecular weight distribution kinetics for ultrasonic reactions of polymers, *AIChE J.* 47 (1997) 2341–2348.
- [19] G.J. Price, P.F. Smith, Ultrasonic degradation of polymer solutions 1. Polystyrene revisited, *Polym. Int.* 24 (1991) 159–164.
- [20] G. Madras, V. Karmore, Continuous distribution kinetics for ultrasonic degradation of poly (methyl methacrylate), *Polym. Int.* 50 (2001) 683–687.
- [21] M.T. Taghizadeh, A. Bahadori, Degradation kinetics of poly (vinyl-pyrrolidone) under ultrasonic irradiation, *J. Polym. Res.* 16 (2009) 545–554.
- [22] A. Mehrdad, Effect of HCl and solution concentration on the ultrasonic degradation of aqueous solution of poly (ethylene oxide), *J. Polym. Eng.* 28 (2008) 597–610.
- [23] A. Mehrdad, M.R. Rostami, Effect of temperature and concentration of H₃O⁺ ions on the intrinsic viscosity of poly (ethylene oxide) in aqueous solutions, *Fluid Phase Equilib.* 268 (2008) 109–113.
- [24] M.T. Taghizadeh, A. Mehrdad, Ultrasonic degradation of solutions of poly (vinyl acetate) in tetrahydrofuran, *J. Appl. Polym. Sci.* 96 (2005) 2373–2376.
- [25] M.T. Taghizadeh, A. Mehrdad, Calculation of rate constants for the ultrasonic degradation of aqueous solutions of polyvinyl alcohol by viscometry, *Ultrason. Sonochem.* 10 (2003) 309–313.
- [26] N. Daraboina, G. Madras, Kinetics of the ultrasonic degradation of poly (alkyl methacrylates), *Ultrason. Sonochem.* 16 (2009) 273–279.
- [27] V.K. Konaganti, G. Madras, Ultrasonic degradation of poly (methyl methacrylate-co-alkyl acrylate) copolymers, *Ultrason. Sonochem.*, doi:10.1016/j.ultsonch.2009.08.016.
- [28] G. Madras, S. Kumar, S. Chattopadhyay, Continuous distribution kinetics for ultrasonic degradation of polymers, *Polym. Degrad. Stab.* 69 (2000) 73–78.
- [29] P.N. Songkhla, J. Woothikanokkhan, Effect of the copolymer composition on the *K* and *a* constants of the Mark–Houwink equation: styrene–methyl methacrylate random copolymers, *J. Polym. Sci. Part B* 40 (2002) 562–571.
- [30] A.M. Aredts, J.W. de Hann, A.L. German, G.P.M. van der Velden, Characterization of intramolecular microstructure of styrene–methyl methacrylate copolymers: new proton NMR assignments supported by 2D-NOESY NMR, *Macromolecules* 24 (1991) 1473–1479.
- [31] R. Vijayaraghavan, M. Surianarayanan, K.V. Raghavan, Studies on synthesis and characterization of charge transfer polymerization of styrene and alkyl methacrylates, *J. Macromol. Sci. Chem. Part A* 40 (2003) 1057–1080.
- [32] F.A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, second ed., Academic Press, San Diego, 1988.
- [33] C.J. Pouchert, *The Aldrich Library of NMR Spectra*, second ed., Aldrich Chemicals, Milwaukee, 1983.
- [34] N.K. Vaill, J.W. Barlow, J.J. Beaman, H.L. Marcus, D.L. Bourell, Development of a poly(methyl methacrylate-co-*n*-butyl methacrylate) copolymer binder system, *J. Appl. Polym. Sci.* 52 (1994) 789–811.
- [35] T. Kelen, F. Tudos, Analysis of the linear methods for determining copolymerization reactivity ratios. I. A new improved linear graphic method, *J. Macromol. Sci. Chem.* 9A (1975) 1–27.
- [36] J. Bandrup, E.H. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1975.

- [37] T. Ozawa, A new method of analyzing thermogravimetric data, *Bull. Chem. Soc. Jpn.* 38 (1965) 1881–1886.
- [38] R. Vijayaraghavan, M. Surianarayanan, R.P. Gangadara, K.V. Raghavan, Influence of molecular weight and tacticity on thermal stabilities of hydroquinone promoted CT polymerization of styrene and alkylmethacrylates, *Eur. Polym. J.* 36 (2000) 2569–2579.
- [39] P. Tordjeman, L. Teze, J.L. Halary, L. Monnerie, On the plastic and viscoelastic behavior of methylmethacrylate-based random copolymers, *Polym. Eng. Sci.* 37 (1997) 1621–1632.
- [40] N.H. Langton, P. Vaughan, Cavitation and the ultrasonic degradation of high polymers, *J. Appl. Phys.* 13 (1962) 478–482.
- [41] M.T. Taghizadeh, T. Asadpour, Effect of molecular weight on the ultrasonic degradation of poly(vinyl-pyrrolidone), *Ultrason. Sonochem.* 16 (2009) 280–286.
- [42] T.Q. Nguyen, Q.Z. Liang, H. Kasush, Kinetics of ultrasonic and transient elongational flow degradation: a comparative study, *Polymer* 38 (1997) 3783–3793.
- [43] D.R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press LCC, Boca Raton, FL, 1998.
- [44] A.I. Akhmedov, R.I. Ibragimova, *Academy of Sciences of the Azerbaidzhan*, Plenum Publishing Corporation, SSR, 1991.
- [45] J.L. Halary, A.K. Oultache, J.F. Louyot, B. Jasse, T. Sarref, R. Muller, Viscoelastic Properties of styrene-co-methyl methacrylate random copolymers, *J. Polym. Sci. Part B* 29 (1991) 933–943.
- [46] R. Weidisch, G.H. Michler, H. Fischer, M. Arnold, S. Hoffmann, M. Stamm, Mechanical properties of weakly segregated block copolymers: 1. Synergism on tensile properties of poly (styrene-*b*-*n*-butylmethacrylate) diblock copolymers, *Polymer* 40 (1999) 1191–1199.
- [47] Z. Matusinović, M. Rogošić, H.J. Mencer, A correlation of the limiting viscosity number, molecular mass and composition of statistical linear styrene-methyl methacrylate copolymers, *Eur. Polym. J.* 41 (2005) 2934–2944.
- [48] D. Rana, H. Mounach, J.L. Halary, L. Monnerie, Differences in mechanical behavior between alternating and random styrene-methyl methacrylate copolymers, *J. Mater. Sci.* 40 (2005) 943–953.