International Journal of Engineering and Applied Sciences (IJEAS)
ISSN: 2394-3661, Volume-2, Issue-4, April 2015

Synthesis of High Molecular Weight Polystearylacrylate and Polystearylmethacrylate Polymers via ATRP Method as Thermal Energy Storage Materials

Derya Kahraman Döğüşcü, Cemil Alkan

***Abstract*— In this study, poly(stearyl acrylate) (PSA) and poly(stearyl methacrylate) (PSMA) homopolymers were produced via atom transfer radical polymerization (ATRP) method from stearyl acrylate (SA) and stearyl methacrylate (SMA) monomers. Fourier transform-infrared (FT-IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy techniques were used for structural characterization as thermal energy storage characteristics and thermal stability property were determined by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques respectively. The average onset phase transition temperatures of the PSA were measured as 48.1 and 43.5 °C as those of PSMA were measured as 30.8 and 23.5 °C respectively. The averages of latent heats of phase transitions were 100.2 and -81.5 J/g for PSA and 55.8 and -44.8 J/g for PSMA respectively. In addition, PSA and PSMA were found thermally durable up to considerably high temperatures compared to possible ambient temperatures. Molecular weight analysis measurements were performed using gel permeation chromatography (GPC) and number average molecular weights of synthesized polymers was found in the range of 58000-439000 g/mol. Based on the results, PSA and PSMA polymers are potential materials for thermal energy storage applications.**

***Index Terms*— ATRP, phase change material (PCM), polyacrylate, smart polymers, thermal energy storage.**

I. INTRODUCTION

Synthesis of polymers with bulky side groups through conventional free radical polymerization results in low molecular weight products since side groups hinders polymerization sterically. Several controlled/living radical polymerization methods providing ability to synthesize polymers with sufficiently high and predictable molecular weights and vast number of architecturally and compositionally new materials have been developed in the last few decades [1].

ATRP is one of those processes [2], [3]. In this method, polymerization occurs through a reversible activation of dormant polymer chain containing halogen by the metal complex via a one-electron redox reaction [3]. The process for Cu complex as a catalyst is usually introduced by the dynamic equilibrium [4] as shown in the following reaction equilibrium. In this way, the equilibrium between activation and deactivation is established quickly, and then a well controlled polymerization progresses on the landmarks of the polymer chain. Both initiator and transition metal complex are leading factors affecting the equilibrium reaction. The transition metal complex is consisted of a ligand and a metal halide. The ligand around the central metal atom has two effects one of which is the solubility of the complex in the organic media as the other one of which is the reactivity of the redox reaction via the adjustment of the redox potential of the metal [4].

$$P_nX + Cu(I)XL_2 \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^{*} + Cu(II)X_2L_2 \qquad \text{Equation (1)}$$

Where; P is a polymer, X is a halogenide, and L is a monodentate ligand.

Thermal energy storage has became one of the most important issues in energy efficiency due to that storage supports charging and discharging efforts. In case of thermal energy storage, phase change materials (PCMs) are the most attractive ones among the potential materials. They have high storage capacity and small temperature variations during usage [5]. PCMs are commonly applied in many fields such as solar energy storage [6], [7], thermal regulating fabrics [8]-[12], electronic materials [13], building temperature fluctuations control [14], cool storage [15], and so on.

Recently PCM research goes through solid state phase change materials due to no liquid handling problem. Solid-solid polymeric PCMs are promising as solid state PCMs because they are easily processed and formed in desired dimensions.

In this study, PSA and PSMA were synthesized as solid-solid polymeric PCMs via ATRP method to obtain high molecular weight polymeric compounds and their chemical characterization, thermal heat storage properties, thermal durability, and molecular weight distribution were investigated.

II. EXPERIMENTAL

2.1. Materials

In this study, SA and SMA were obtained from Aldrich Company. They were extracted three times with 5% aqueous NaOH solution and then washed with distilled water. Then they are dried over CaH_2 and filtered off drying agent. Cu(I)Br (Acros Organic), $CuBr_2$ (Acros Organic), and ethyl-2-bromoisobutyrate (Alfa Aesar) were used as initiator.

Derya Kahraman Döğüşcü, Chemistry Department, Gaziosmanpaşa University, 60240, Tokat, Turkey, +903562521616-3068.

Cemil Alkan, Chemistry Department, Gaziosmanpaşa University, 60240, Tokat, Turkey, +903562521616-3063.

CuBr (Acros, 98%) and $CuBr_2$ (Acros, 99%) were purified by washing with glacial acetic acid, followed by washing with absolute ethanol and ethyl ether, and then dried under vacuum. N,N,N,N,N-pentamethyl ethylene triamin (Merck) was chosen as a ligand for the Cu-mediated system. Ethyl-2-bromoisobutyrate, N,N,N,N,N-pentamethyl ethylene triamin, and acetone were all used as received.

2.2. Polymerization procedure

Cu(I)Br (39.1 mg, 2.73×10^{-4} mol) and $CuBr_2$ (3 mg, 1.4×10^{-5} mol) were added to a dry capped test tube. The tube was sealed with a rubber septum, degassed and back-filled with nitrogen several times and left under nitrogen. Deoxygenated acetone (1 mL) and momoner (2.7×10^{-2} mol) were added to the tube. Then N,N,N,N,N-pentamethyl ethylene triamin (60 µL, $2{,}9 \times 10^{-4}$ mol) was added to the Cu complex. The formation of the copper complex was revealed by the change of solution color from cloudy and colorless to clear light green. N_2 gas was applied to decrease O_2 level and supply inert atmosphere. After complex formation ethyl-2-bromoisobutyrate (80.7 µL, 5.5×10^{-4} mol) was added to the flask and initial sample was removed. Then the flask was placed in an oil bath thermostated at 70 °C. The polymerizations were progressed for 6, 9 and 24 hours in order to investigate molecular weight development.

2.3. Characterization of PSA and PSMA

PSA and PSMA were characterized chemically using FT-IR (Jasco 430 model) and ^{1}H NMR (BRUKER 400 MHz model) spectrophotometers. Monomers and polymers in deuterated chloroform ($CDCl_3$) were used for ^{1}H NMR analysis with 5% tetramethyl silane (TMS, $Si(CH3)_4$) reference. PSA and PSMA polymers were analyzed thermaly by using Perkin Elmer Jade model DSC instrument. The samples of the polymers were measured with 5 °C/min heating and cooling rates under nitrogen atmosphere. Thermal properties and degradation property of PSA and PSMA polymers were carried out with a TGA analyzer (Perkin Elmer TGA7 model) at a heating rate of 10°C/min in static atmosphere. Using a Malvern Viscoteck GPCmax instrument equipped with a refractive index (Ve 3580 Malvern Dedector) and a light scattering detector (270 Dual Malvern Dedector) number-average molecular weight, weight-average molecular weight, Z-average molecular weight and heterogeneous indices of synthesized polymers in tetrahydrofuran were determined at 35 °C.

III. RESULTS AND DISCUSSION

3.1. Spectroscopic analysis of the PSA and PSMA polymers

The long side chain of SA and SMA monomers are known to play an important role in the kinetic behavior of the radical processes [16]. FT-IR and NMR spectroscopies are commonly used to verify whether the polymers were successfully synthesized or not. Figure 1(a) and Figure 1(b) show FT-IR spectra of SA monomer and PSA polymer synthesized in different polymerization times, respectively. In the spectra of both of the monomers and the polymers, -CH stretching peaks specific to alkyl chains have been observed between 2850 and 3100 cm^{-1}. The peaks observed at 1726 and 1736 cm^{-1} represent carboxyl peaks of SA and PSA respectively. Methoxy peaks of the monomers and the polymers were at 1197 cm^{-1} and 1165 cm^{-1}, respectively. Furthermore, the vibration band of C=C vinyl group of SA at 1632 cm^{-1} was absent in PSA due to polymerization.

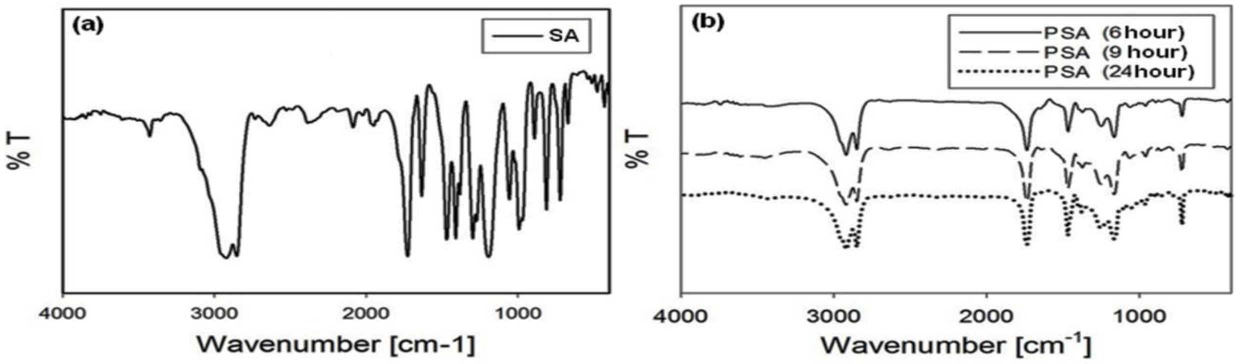

Figure 1. FT-IR spectra of SA (a) and PSA (b)

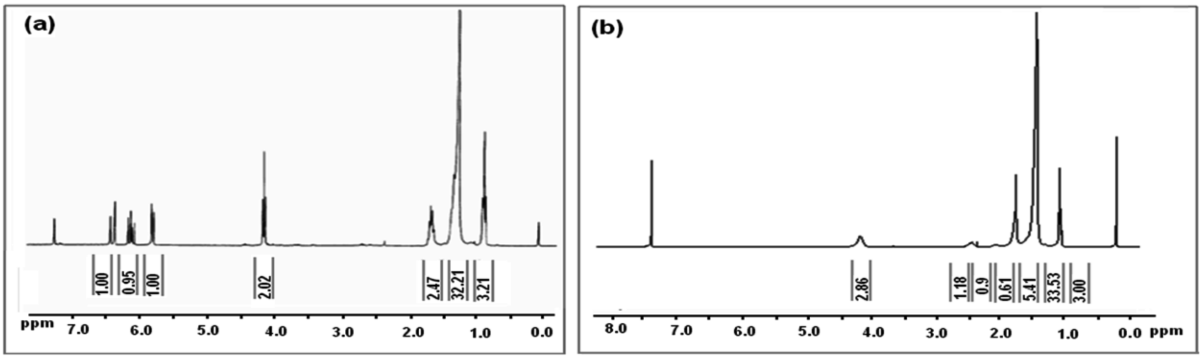

Figure 2. ^{1}H-NMR spectra of SA (a) and PSA (b) (24 hours)

Figure 2(a) and Figure 2(b) show ^{1}H NMR spectra of SA and PSA. Herein, C=C double bond peaks were found between 5.5 and 6.4 ppm. They disappeared after polymerization as expected. It is proving that majority of vinyl monomers contributed to polymers as a result of the polymerization reaction. Besides, the number of H protons and chemical shifts were in good agreement with PSA and PSMA and all results confirmed that the polymers were successfully synthesized.

3.2. Evaluation of DSC thermograms of the PSA and PSMA polymers

The long side chains of PSA or PSMA influence the crystallization of the polymer in spite that the backbone is mainly syndiotactic [17]. Performance of the final materials is dependent on the structural features of the macromolecules [18]. Therefore, a suitable strategy allowing the synthesis of desired macrostructures is essential to get the expected properties of the materials.

Phase change temperature and latent heat storage capacity are the most important characteristics of PCMs. DSC analyses of the polymers reveal the thermophysical characteristics of PSA and PSMA. Figure 3 shows thermograms of the polymers as Table 1 is tabulating the data from those graphs.

According to DSC analysis, manufactured polymers are thermally stable at possible ambient temperatures and have reversible phase change behaviors. The self-associated pendant alkyl chains form small crystalline domains in the matrix and these domains realize crystalline-amorphous transformations during phase change process [19].

Phase change of PSA and PSMA occurs in the ranges of 48.2-48.4 °C and 25.9-33.4 °C during heating respectively and in the ranges of 43.4-43.6 °C and 20.5-21.0 °C during cooling respectively. Besides PSA and PSMA have phase transition enthalpy of 88.9-107.7 J/g and 38.4-83.8 J/g, and crystallization enthalpy of 75.6-88.3 J/g and 39.5-51.5 J/g respectively. Samples polymerized to almost full conversion remained at solid state before and after phase change temperature with no evidence of phase separation. It can be inferred that side chain microcrystalline domains were distributed in the matrices. Crystalline-amorphous or amorphous-crystalline transformations occurred in these domains when heated or cooled respectively. Some authors reported that outside reactions as generation and recombination of radicals in pendant alkyl chains could lead to a chemically cross-linking [20], [21]. However, under our polymerization conditions, all the samples were found completely soluble in THF at room temperature.

Table 1. Thermal energy storage characteristics of PSA and PSMA using DSC analysis method

	Heating Period		Cooling Period	
Polymers	Solid-solid phase change temperature (^{o}C)	Latent heat (J/g)	solid-solid phase change temperature (^{o}C)	Latent heat (J/g)
PSA (6 hours)	48.4	88.9	43.6	-75.6
PSA (9 hours)	48.2	103.9	43.5	-88.3
PSA (24 hours)	47.8	107.8	43.4	-80.4
PSMA (6 hours)	25.9	38.4	20.9	-39.5
PSMA (9 hours)	33.1	45.2	20.9	-43.3
PSMA (24 hours)	33.43	83.79	28.46	-51.48

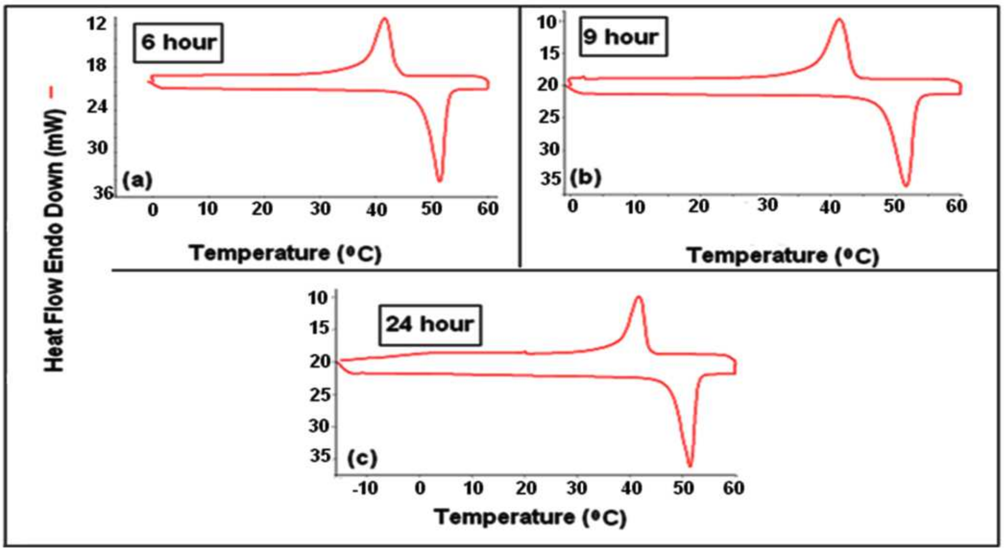

Figure 3. DSC thermograms of PSA

PSA and PSMA are physically solid materials below and above phase transition temperature at which latent heat energy storage occurred. The morphology change behavior was reproducible in consecutive cooling/heating cycles, proposing the possible uses of these polymers as solid-solid PCMs.

3.3. Thermal durability of PSA and PSMA polymers

Thermal durability is another important factor for exploitation of PCMs.

Thermal degradation characteristics or thermal durability of PCMs can be determined using TGA.

TGA and differential TGA (DTG) curves of PSA are given in Figure 4 and the data from both of PSA and PSMA curves are tabulated in Table 2. According to drawn curves, synthesized polymers degrade in one step in the range of 280-456 °C and 233-414 °C for PSA and PSMA, respectively. Degradation characteristics of both of the polymers are similar to each other as expected. Since the initial degradation temperatures are fairly high, PSA and PSMA can be considered as potential materials for PCM applications.

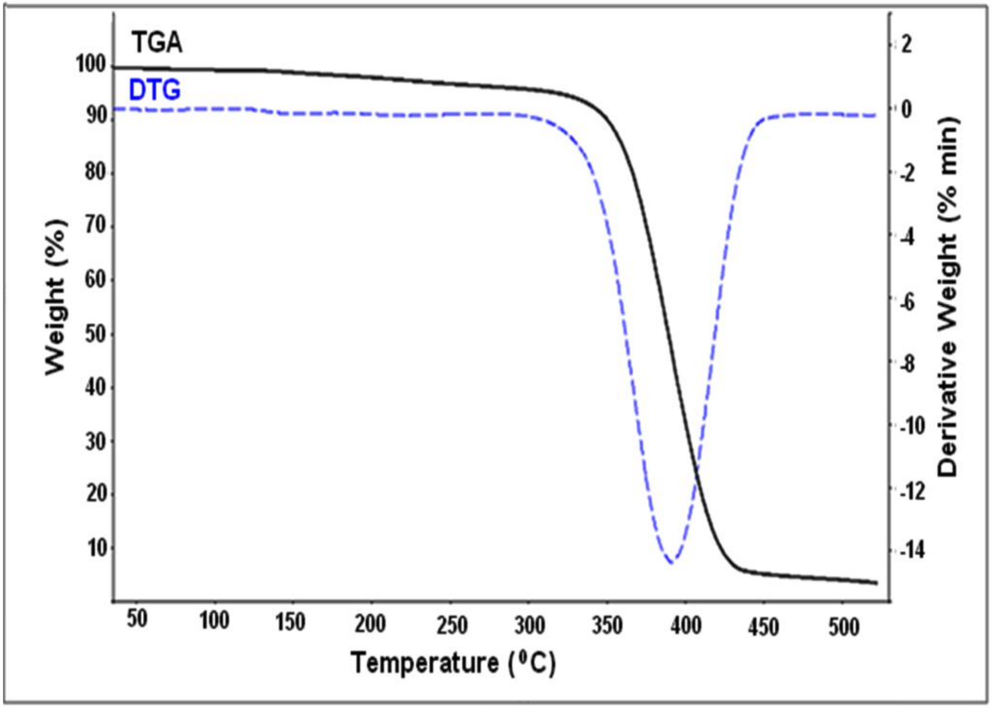

Figure 4. TG curves of PSA (24 hours)

Table 2. TGA results of PSA and PSMA

Material	First degradation temperature range (°C)	Weight loss (%)	DTG$_{max}$	5% Weight loss (°C)
PSA (24 hours)	280-456	94.79	391	287
PSMA (24 hours)	233-414	78.58	315	95

Molecular weight analyses of PSA and PSMA polymers

Molecular weight and molecular weight distribution are important criterions for bulky sided polymers. It is known that bulky sides are like branches causing decrease in viscosity of the polymers. However the higher the molecular weight, the stiffer, the matrix is. This brings the material through solid in structure. In other words, polymers at high molecular weights behave as solid-solid phase change materials instead of solid-liquid or solid-high viscosity liquid. Figure 5 shows molecular weight distribution of PSA as a sample. The GPC data are also tabulated in Table 3. It is clear from the table that PSA and PSMA can be prepared by ATRP method at considerably high molecular weights up to sufficient to hold the matrix in solid.

A polymer can be obtained with a narrow molar mass distribution, when some requirements that are specific to each polymerization system are fulfilled. Several studies have been reported on this subject. There are five major conditions [22]–[24]: (1) negligible chain transfer or termination, (2) the higher rate of propagation than the rate of depropagation, (3) the rate of propagation at least as fast as the rate of initiation, (4) the sufficiently fast equilibrium created in the intermediate during the reaction, and (5) the homogeneity of the system supplied with vigorous agitation. Under the conditions mentioned, the polydispersity (Mw/Mn) is expected to decrease with conversion. The only condition that it increases, the chain breaking reactions occur. The polymerization in this work has been performed at low temperature and pure reaction conditions to get linear and low polydispersity polymers. The synthesis of such polymers is proven by GPC data and remarkable solubility of them in tetrahydrofuran as solvent.

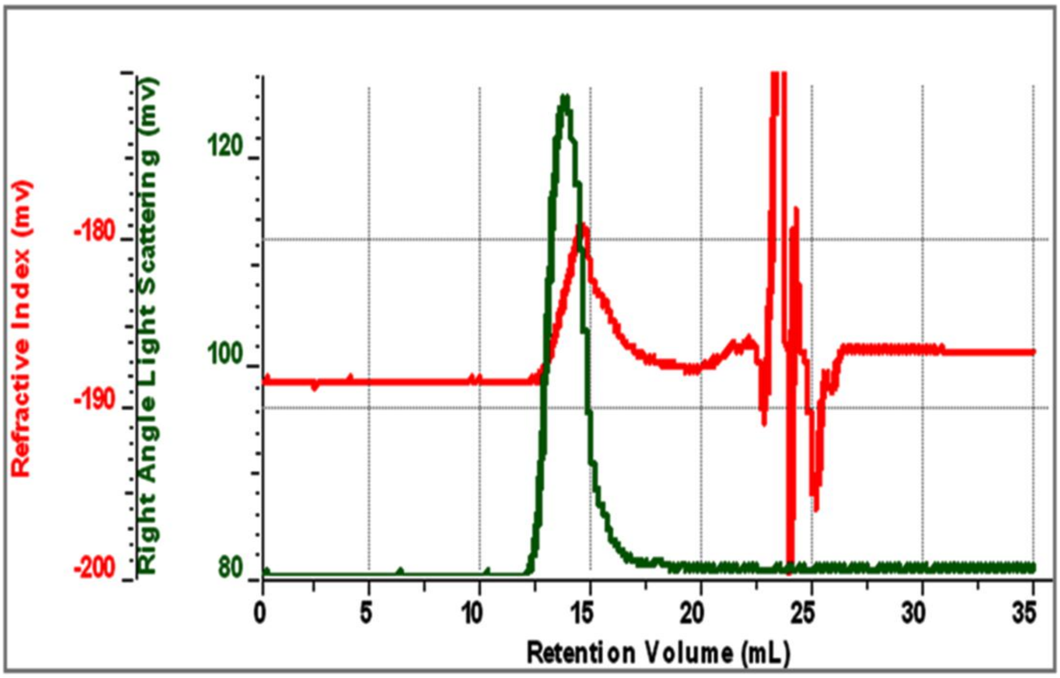

Figure 5. GPC spectra of PSA (24 hours)

Table 3. GPC results of PSA and PSMA

Polymers	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	HI
PSA (6 hours)	439000	798000	1.495×10^6	1.82
PSA (9 hours)	58000	237000	545000	4.08
PSA (24 hours)	241000	580000	1.29×10^6	2.40
PSMA (6 hours)	78000	493000	1.39×10^6	6.32
PSMA (9 hours)	85000	120000	192000	1.41
PSMA (24 hours)	195000	590000	1.01×10^6	3.02

IV. CONCLUSIONS

It is shown that polymerization method presented in this study was quite successful to produce solid-solid polymeric PCMs with enhanced material properties. FT-IR and ^{1}H-NMR results have proved successfully manufactured polymers via ATRP method. According to the GPC results, fabricated polymers have considerably high molecular weights which brought about solid state consistency above phase transition temperature. Thermal energy storage potential of the polymers is considerably high as compared to literature materials. PSA and PSMA are durable up to 250 °C that is considerably higher than possible ambient temperatures. By taking into consideration of all results, it was concluded that the prepared polymers could be considered as promising PCMs with no liquid problem and easy material processing advantage for temperature regulating applications.

Results obtained in this study can be extended to different types of poly(n-alkyl acrylates) and poly(n-alkyl methacrylates).

ACKNOWLEDGEMENTS

The author would like to acknowledge financial support by Gaziosmanpaşa University Scientific Research Funds (The Project Code: BAP2012/03).

REFERENCES

[1] K. A. Davis, K. Matyjaszewski, “Atom Transfer Radical Polymerization of *tert*-Butyl Acrylate and Preparation of Block Copolymers,” *Macromolecules*, vol. 33(11), pp. 4039-4047, 2000.
[2] J.S. Wang, K. Matyjaszewski, “Controlled "Living" Radical Polymerization. Atom Transfer Radical Polymerization in the resence of Transition-Metal Complexes,” *Journal of The American Chemical Society*, vol. 117(20), pp. 5614-5615, 1995.
[3] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, “Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris-(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization,” *Macromolecules,* vol. 28(5), pp. 1721-1723, 1995.
[4] K. Matyjaszewski, J. Xia, “Atom Transfer Radical Polymerization,” *Chemical Reviews,* vol. 101(9), pp. 2921–2990, 2001.

[5] L. Sanchez-Silva, J. F. Rodriguez, A. Romero, A. M. Borreguero, M. Carmona, P. Sanchez, “Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerization,” *Chemical Engineering Journal,* vol. 157(1), pp. 216-222, 2010.
[6] Y. Tian, C.Y. Zhao, “A numerical investigation of heat transfer in phase change materials (PCMs) embedded in porous metal,” *Energy,* vol. 36(9), pp. 5539-5546, 2011.
[7] C. Alkan, Y. Tek, D. Kahraman, “Preparation and characterization of a series of thiourea derivatives as phase change materials for thermal energy storage,” *Turkish Journal of Chemistry*, vol. 35, pp. 769-777, 2011.
[8] X.Y. Gao, N. Han, X.X. Zhang, W.Y. Yu, “Melt-processable acrylonitrile-methyl acrylate copolymers and melt-spun fibers containing MicroPCMs,” *Journal of Materials Science*, vol. 44(21), pp. 5877-5884, 2009.
[9] F. Salaün, E. Devaux, S. Bourbigot, P. Rumeau, “Development of phase change materials in clothing Part I: Formulation of microencapsulated phase change,” *Textile Research Journal*, vol. 80(3), pp. 195-205, 2010.
[10] E. Onder, N. Sarier, E. Cimen, “Encapsulation of phase change materials by complex coacervation to improve thermal performances of woven fabrics,” *Thermochimica Acta*, vol. 467(1-2), pp. 63-72, 2008.
[11] S. Alay, C. Alkan, F. Göde, “Steady-state thermal comfort properties of fabrics incorporated with microencapsulated phase change materials,” *The Journal of The Textile Institute*, vol. 103(7), pp. 757-765, 2012.
[12] S. Alay, C. Alkan, F. Gode, “Synthesis and characterization of poly(methyl methacrylate)/n-hexadecane microcapsules using different cross-linkers and their application to some fabrics,” *Thermochimica Acta*, vol. 518(1-2), pp. 1-8, 2011.
[13] W.B. Jackson, R.D. Gould, J.C. Mulligan, “Performance of an octacosane based micropcm fluid for cooling EV electronics,” 8th AIAA/ASME Joint Thermophysics and Heat Transfer Conference. St. Louis, Missouri, 2002.
[14] F. Kuznik. J. Virgone, “Experimental assessment of a phase change material for Wall building use,” *Applied Energy*, vol. 86(10), pp. 2038-2046, 2009.
[15] B. He, F. Setterwall, “Technical grade paraffin waxes as phase change materials for cool thermal storage and cool storage systems capital cost estimation,” *Energy Conversion and Management*, vol. 43(13), pp. 1709–1723, 2002.
[16] G. E. Scott, E. Senogles, “Polymerization Kinetics of n-Lauryl Acrylate,” *Journal of Macromolecular Science: Part A – Chemistry*, vol. 4(5), pp. 1105-1117, 1970.
[17] H.W.S. Hsieh, B. Post, J. Morawest, “A crystallographic study of polymers exhibiting side chain crystallization,” *Journal of Polymer Science: Polymer Physics Edition*, vol. 14(7), pp. 1241-1255, 1976.
[18] X. Zhu, Y. Gu, Z. Cheng, J. Lu, “Synthesis of poly(octadecyl acrylate-b-styrene-b-octadecyl acrylate) triblock copolymer by atom transfer radical polymerization,” *Journal of Applied Polymer Science*, vol. 93(4), pp. 1539-1545, 2004.
[19] E. Hempel, H. Huth, M. Beiner, “Interrelation between side chain crystallization and dynamic glass transitions in higher poly(n-alkyl methacrylates),” *Thermochimica Acta*, vol. 403(1), pp.105−114, 2003.
[20] M. Lazár, L. Hrčková, A. Fiedlerová, E. Borsig, “Crosslinking during radical polymerization of dodecyl methacrylate,” *Macromolecular Materials and Engineering*, vol. 283(1), pp. 88−92, 2000.
[21] M. Lazár, L. Hrčková, A. Fiedlerová, E. Borsig, “Polymerization of n-dodecyl metracrylate into high conversion,” *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, vol. 39(5), pp. 365−377, 2002.
[22] H. L. Hsieh, R. P. Quirk, “Anionic Polymerization Principles and Practical Applications”, Marcel Dekker Inc, ISBN 0-8247-9523-7, New York, 1996.
[23] K. Matyjaszewski, S. Gaynor, J.S. Wang, “Controlled Radical Polymerizations: The Use of Alkyl Iodides in Degenerative Transfer,” *Macromolecules,* vol. 28(6), pp. 2093-2095, 1995.
[24] J. Qiu, B. Charleux, K. Matyjaszewski, “Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems,” *Progress in Polymer Science*, vol. 26(10), pp. 2083-2134, 2001.

ABOUT THE AUTHOR

Derya Kahraman Döğüşcü has a master of science degree in chemistry at Gaziosmanpaşa university of Turkey where she is going on her PhD in physical chemistry. She has experience on synthesis and preparation of polymeric materials and systems for thermal energy storage and 7 publications.

Dr Cemil Alkan has a master degree in chemistry and PhD in polymer science and technology at Middle East Technical University of Turkey. He has been a research and education staff since 2004 at Gaziosmanpaşa university of Turkey. He has 57 papers of materials especially polymers, polymeric blends, and composites. He has mainly interested in thermal energy storage materials and functional fibers.