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Synthesis, Characterization and Thermal Properties of Green ABC Miktoarm Star Terpolymers

Rabab M. Nasser[1,2], *Amal M. Nassar*[2]

[1] *Chemistry Department, University College of Samtah, Jazan University, Saudi Arabia*
[2] *Egyptian Petroleum Research Institute, Department of Petroleum Applications, Nasr city, Cairo, Egypt*

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Abstract

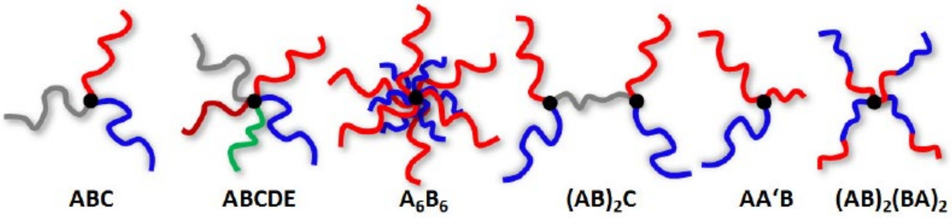
Six (Jojoba-Divinyl Benzene–Alkylacrylate) and five (jojoba–divinyl benzene–α-olefins) ABC miktoarm star terpolymers were prepared by free radical polymerization using (1: 0.2: 1.8) molar ratios. The prepared terpolymers were characterized using FT-IR and ^{1}H-NMR analysis. The weight average molecular weight Mw, the number average molecular weight Mn and the poly-dispersity index PDI were determined from GPC (gel permeation chromatography). Thermal properties (DSC and TGA analysis) of the prepared terpolymers were determined. The morphology of the prepared star polymers were done using SEM (Scanning Electron Microscopy).

Keywords: *Miktoarm Star polymers; jojoba; divinyl benzene; alkylacrylate; thermal analysis; SEM.*

1. Introduction

The preparation of polymers with well-defined forms of branching has posed a challenge to polymer chemists for many years. Star-branched polymers consisting of several linear chains linked together at one end of each chain constitute the simplest form of branching. Perhaps the earliest attempt to synthesize such molecules was that of Shaefgren and Flory [1]; who polymerized e-caprolactam in the presence of either a tetra-functional or an octa-functional carboxylic acid to produce polymers of the type $(R\text{ -}CO(NH(CH_2)_5\,CO)n\text{-}OH)_x$ where $x = 4$ or 8. Another technique has been used which involves divinylbenzene as coupling agent [2-4]. Star-shaped polymers are characterized as structures in which all the chains of a molecule are linked together to a small-molar-mass core. The interest in star polymers arises not only from the fact that they are models for branched polymers but also from their enhanced segment densities [5].

Miktoarm star polymers, in general, are defined as star polymers with at least three arms of molecular weight, chemical or topological asymmetry (Scheme 1) [6]. Various review articles dealing with the synthesis of miktoarm star polymer systems were published during the last two decades, highlighting the interest in such complex materials and their high potential [6-11]. However, in the following, the main focus will be set on ABC miktoarm star terpolymers, which display the corresponding branched analogues of the intensively studied linear ABC triblock terpolymers [12- 18].



Scheme 1. Examples of miktoarm star polymers with chemical (ABC, ABCDE, A_6B_6, $(AB)_2C$)), molecular weight (AA`B) or topological asymmetry ($(AB)_2(BA)_2$).

In the present work, eleven miktoarm stars branched terpolymers were prepared by free radical polymerization and elucidated using FT-IR, ^{1}H-NMR, and the average molecular weight was determined using GPC. Thermal analysis (DSC and TGA) were determined; while morphologies of polymers surface were determined using SEM.

2. Experimental

2.1. Materials

Divinylbenzene (DVB), 79%, acrylaic acid 97%, octyl alcohol 98.0%, decyl alcohol 99.0%, dodecylaclcohol 98.0%, tetradecyl alcohol 97.0%, hexadecyl alcohol 98.0%, octadecyl alcohol 97%, 1-octene 98%, 1-dodecene 99%, 1-tetradecene, 97 %, 1-hexadecene 99 %, benzoyl peroxide 98%, *p*- toluene sulphonic acid hydrated 97%, *p*- hydroquinone 99% were from Sigma-Aldrich Chemical Company; while jojoba oil was obtained from the Egyptian Company of Natural Oils, Egypt.

2.2. Instrumentation

The molecular weight of the prepared terpolymers was determined by using Agilent GPC/SEC, Germany Poly Strogel, particle size 100, 104, 105A°, using tetra-hydro-furan "THF" as a solvent. Differential scanning calorimetric thermos-grams were recorded using Simultaneous Q-600 DSC/TGA (USA). Calculations were made based on the corrected sample weight. Fourier Transform Infrared (FTIR) spectra were determined using FTIR- spectrometer, Model Type Mattson Infinity series Bench Top 961. ^{1}H-NMR Spectrometer Type (300MHz Spectrophotometer- W-P-300, Bruker), using tetra-methyl silane "TMS" as internal standard and dimethyl sulphoxide "DMSO-D_6" as a solvent. The microscopic characterization of polymers was carried out using scanning electron microscope (JEOL JSM-5410, Japan). The energy of the acceleration beam employed was 30 KV. All micrographs were taken at a magnification power (X 500).

2.3. Methods and procedures:

2.3.1. Synthesis of alkylacrylate

Octylacrylate, decylacrylate, dodecylacrylate, tetradecylacrylate, hexadecylacrylate, and octadecylacrylate were prepared as mentioned at literature [19-24].

2.3.2. Synthesis of (Jojoba- DVB- alkylacrylate) miktoarm star terpolymers.

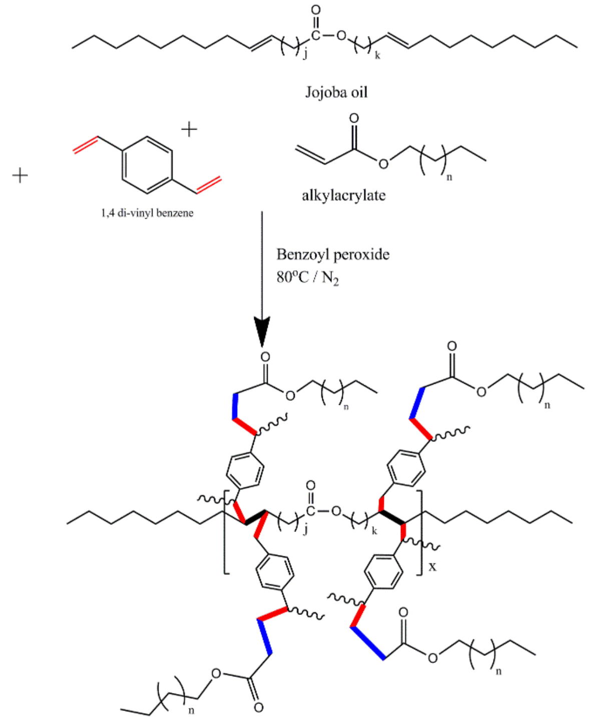
In 250mL three necked bottomed flask provided with a magnetic stirrer and N_2 inlet, 1mole of jojoba was added to 0.2mole of DVB and 1.8mole of alkylacrylate; the alkylacrylate used were (octylacrylate, decylacrylate, dodecylacrylate, tetradecylacrylate, hexadecylacrylate and octadecylacrylate) separately, the desired amount of benzoyl peroxide was used at 80±10°C. After the completion of the reaction, the product was poured drop by drop in cooled methanol, filtered off and dry, Scheme 2.

2.3.3. Synthesis of (Jojoba- DVB- α olefins) miktoarm star terpolymers.

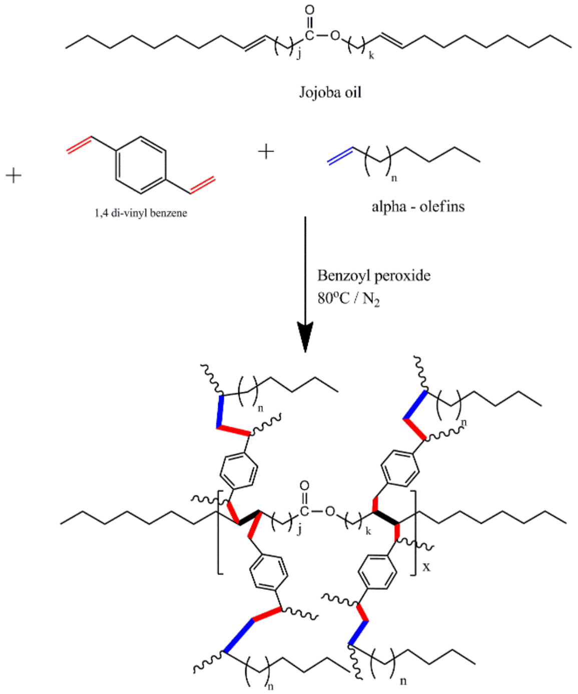
In 250mL three necked bottomed flask provided with a magnetic stirrer and N_2 inlet, 1mole of jojoba was added to 0.2mole of DVB and 1.8mole of α-olefins; the α-olefins used were (octene, dodecene, tetradecene, hexadecane, and octadecene) separately, the desired amount of benzoyl peroxide was used at 80±10°C. After the completion of the reaction, the product was poured drop by drop in cooled methanol, filtered off and dry, Scheme 3.

3. Results and discussion

Eleven miktoarm terpolymers were prepared by free radical polymerization using jojoba, alkylacrylate, α-olefins and technical grade divinylbenzene DVB, and benzoyl peroxid (BPO) as initiator at 80±10°C. The terpolymers symbol, designation, feed ratio (%), and the actual composition (%) of the prepared terpolymers are given at Table 1.



Scheme 2. (Jojoba- DVB- alkylacrylate) miktoarm star terpolymers



Scheme 3. (Jojoba- DVB- olefins) miktoarm star terpolymers

Table 1. Miktoarm terpolymers symbol, designation, feed ratio (%), and the actual composition (%) of the prepared terpolymers

Symbol	Terpolymer designation	Feed ratio (%)	Terpolymers composition (%)	Symbol	Terpolymer designation	Feed ratio (mole)	Terpolymers composition (%)
A_1	Jojoba: DVB: octylacrylate	33.53: 6.67: 60.00	30: 6.20: 63.80	B_1	Jojoba: DVB: Octene	33.53: 6.67: 60.00	32.12: 6.60: 61.28
A_2	Jojoba: DVB: decylacrylate		27.90: 6.30: 65.90	B_2	Jojoba: DVB: dodecene		30.32: 6.54: 63.14
A_3	Jojoba: DVB: dodecylacrylate		26.12: 6.46: 67.42	B_3	Jojoba: DVB: tetradecene		28.16: 6.42: 65.42
A_4	Jojoba: DVB: tetradecylacrylate		24.68: 6.64: 68.68	B_4	Jojoba: DVB: hexadecane		25.46: 6.20: 68.34
A_5	Jojoba: DVB: hexadecylacrylate		21.86: 6.86: 71.28	B_5	Jojoba: DVB: Octadecene		24.60: 6.12: 69.28
A_6	Jojoba: DVB: octadecylacrylate		20.66: 6.98: 72.36				

3.1. Characterization of the prepared ABC Miktoarm star polymers

The prepared Miktoarm star terpolymers were characterized using GPC (SEC), thermal analysis (DSC and TGA), microscopic characterization (SEM), structural characterization using (^{1}H-NMR and FTIR).

3.1.1. Chromatographic characterization of the prepared terpolymers.

The prepared terpolymers were characterized using GPC/SEC chromatography, Table 2. It was found that the molecular weight increase with increasing the chain length of both alkylacrylate and α-olefin used.

Table 2. Mean molecular weight (Mn), average molecular weight (Mw) and poly dispersity index (PDI) of the prepared Miktoarm terpolymers

Terpolymer designation	Mn	Mw	PI	Terpolymer designation	Mn	Mw	PDI
A_1	16660	26656	1.60	B_1	1363	1664	1.22
A_2	18984	31893	1.68	B_2	1412	1765	1.25
A_3	20778	38231	1.84	B_3	1496	1900	1.27
A_4	24556	52059	2.12	B_4	1541	2034	1.32
A_5	27641	67306	2.435	B_5	1583	2216	1.40
A_6	32534	81335	2.5				

3.1.2. Thermal analysis

Thermal analysis refers to a variety of techniques in which a property of a sample is continuously measured as the sample is programmed through a predetermined temperature profile. Among the most common techniques are thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) [25].

3.1.2.1. TGA analysis

Jojoba: DVB: alkylacrylate and Jojoba: DVB: α-olefin (33.33: 6.67: 60) miktoarm terpolymers were subjected to thermal degradation in air at heating rate 10°C/min., from room temperature to 700°C and results have been summarized in Tables 3 and 4. Initial degradation temperature (IDT), the temperature at 30%, 50%, 70% decomposition of (A_1-A_6) and (B_1-B_5), and integral procedural decomposition temperature (IPDT, a relative measure of thermal stability) were determined. As noticed from Tables (3, 4), star polymers based on alkylacrylate are more stable than that prepared from α- olefins, and as the chain length increases the thermal stability decrease. It can be explained that as the length of alkyl chain increases in the backbone of C–C bond, the bond dissociation energy of the chain decreases and flexibility of the chain increases thus making the polymeric chain more susceptible towards thermal degradation.

Table 3. Thermal properties of Jojoba: DVB: alkylacrylate terpolymers.

Jojoba %	DVB %	Alkylacrylate %	IDT (°C)	Temperature (°C) at weight loss			IPDT (°C)
				T_{30}	T_{50}	T_{70}	
33.33	6.67	Octylacrylate (60)	310	339	373	397	420
33.33	6.67	Decylacrylate (60)	307	364	387	401	410
33.33	6.67	Dodecylacrylate (60)	306	344	371	388	408
33.33	6.67	Tetradecylacrylate (60)	303	353	379	398	407
33.33	6.67	Hexadecylacrylate (60)	296	371	390	405	406
33.33	6.67	Octadecylacrylate (60)	290	336	366	386	396

Table 4. Thermal properties of Jojoba: DVB: α-olefin terpolymers.

Jojoba %	DVB %	α-olefin %	IDT (°C)	Temperature (°C) at weight loss			IPDT (°C)
				T_{30}	T_{50}	T_{70}	
33.33	6.67	Octene (60)	307	375	392	407	406
33.33	6.67	Dodecene (60)	288	327	370	388	404
33.33	6.67	Tetradecene (60)	141	185	353	388	402
33.33	6.67	Hexadecene (60)	109	195	323	380	400
33.33	6.67	Octadecene (60)	95	262	364	391	388

3.1.2.2. DSC

By studying Figures (1 and 2) there were small endothermic peaks around 370°C-380°C, this is the temperatures which were required to break the polymer backbone, and these prove the stability of the prepared polymers toward thermal degradation.

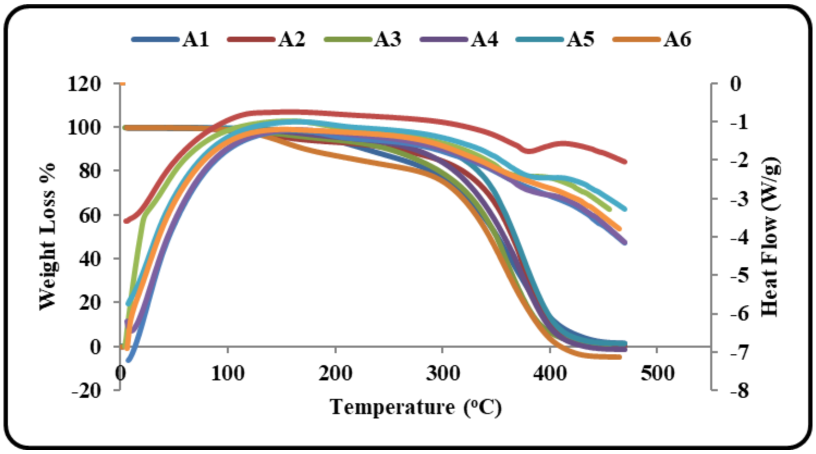


Figure 1. TGA and DSC analysis of (A_1-A_6) star polymers

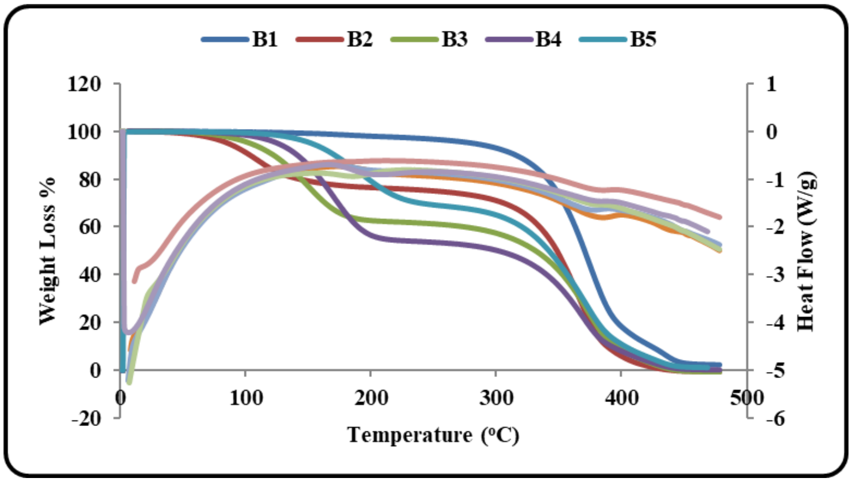


Figure 2. TGA and DSC analysis of (B_1-B_5) star polymers

3.1.3. Surface morphology (SEM)

The prepared star polymers were subjected to surface morphology study by scanning electron microscopy. Terpolymers prepared in the presence of alkylacrylate and α-olefins were cut by a sharp blade at liquid nitrogen temperature, Figure 3.

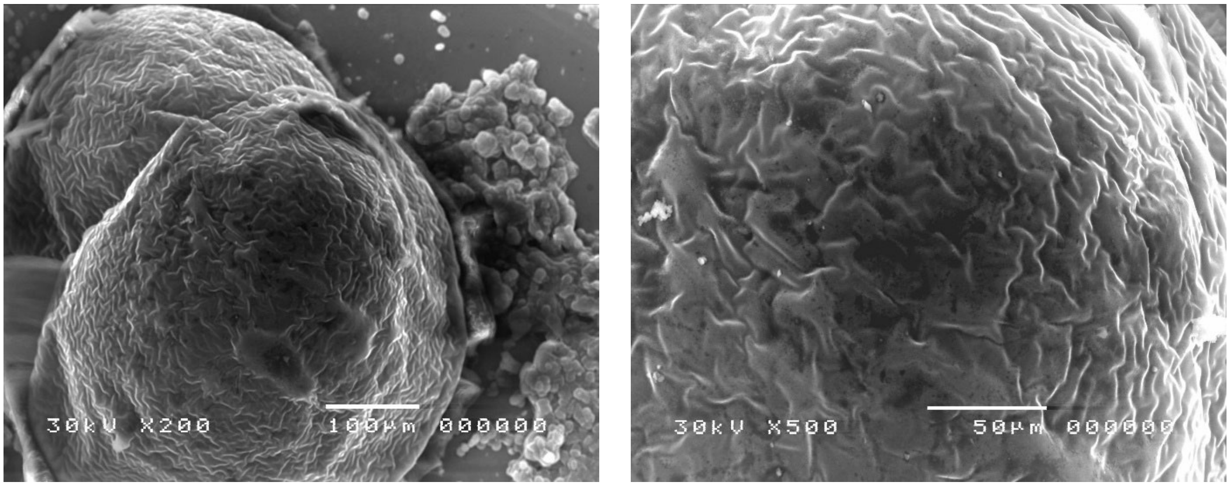


Figure 3. Surface morphology of A_6 miktoarm terpolymer

3.1.4. Structural characterization

3.1.4.1. FT-IR

Characteristic absorption bands of jojoba-DVB-alkylacrylate terpolymers were observed in the FTIR spectra. IR spectra show absorption due to phenyl ring of DVB (aromatic C–H stretching) and aliphatic C–H stretching, characteristics IR peaks of C=O (carbonyl) and C–O–C (esters) confirming the incorporation of alkylacrylates in jojoba chains Sharp peaks of aromatic ring chain vibration, C–O vibration and disubstituted aromatic ring C–H bending vibration was also observed in FTIR spectra of terpolymers Table 5.

Table 5. IR data of the prepared (A_1-A_6) and (B_1-B_5) miktoarm terpolymers

Symbol	Aliphatic (CH –stretching cm^{-1})	Carbonyl stretching cm^{-1})	C-O-C stretching cm^{-1})	Aromatic (C – C stretching cm^{-1})	Ring C-H bending cm^{-1}
A_1	2930	1736	1174	1460	720
A_2	2925	1735	1178	1459	720
A_3	2929	1736	1171	1460	720
A_4	2938	1736	1172	1460	720
A_5	2929	1736	1172	1460	720
A_6	2930	1735	1170	1462	721
B_1	2925	1738	1174	1459	719
B_2	2940	1736	1175	1459	721
B_3	2924	1738	1174	1459	719
B_4	2945	1739	1174	1643, 1460	720
B_5	2925	1739	1174	1640, 1459	721

3.1.5. ^{1}H-NMR

The structure of the prepared miktoarm terpolymers was confirmed by using ^{1}H-NMR, as in Figure 4, ^{1}H-NMR spectrum of (A_1), it was found characteristics peak signals corresponding to (δ-0.90 for ($-CH_3$), δ-4.13 for ($-O-CH_2$), δ-2.53 for – ($CO - CH_2$)) of alkyl acrylate, (δ-2.27 for – ($COO - CH_2$), δ-1.29 for – $(CH_2)_{j\ and\ k}$ -, δ-0.88 for)of jojoba oil, and peak signals around δ- 7.02-7.25 corresponding to phenyl group of DVB. Figure 5; illustrates the spectrum of B_1 as an example of the olefins star polymers. It was found a characteristic peak signals at δ-0.88 for $-CH_3$, δ-$CH_{\underline{2}} - CH_3$, δ-1.25 – $(CH_2)_n$-, δ-2.55 –CH-Ph., δ-1.54 – (CH_2- CH- Ph.) (δ-2.27 for – ($COO - CH_2$), δ-1.29 for – $(CH_2)_{j\ and\ k}$ -, δ-0.88 for)of jojoba oil, and peak signals around δ- 7.02-7.25 corresponding to phenyl group of DVB.

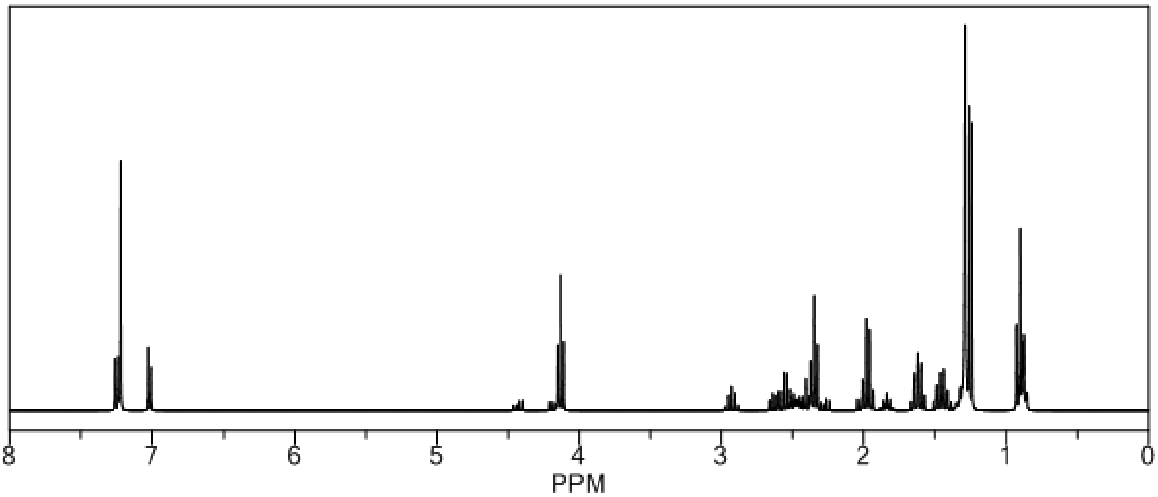


Figure 4. ^{1}H-NMR spectrum of the A_1 terpolymer.

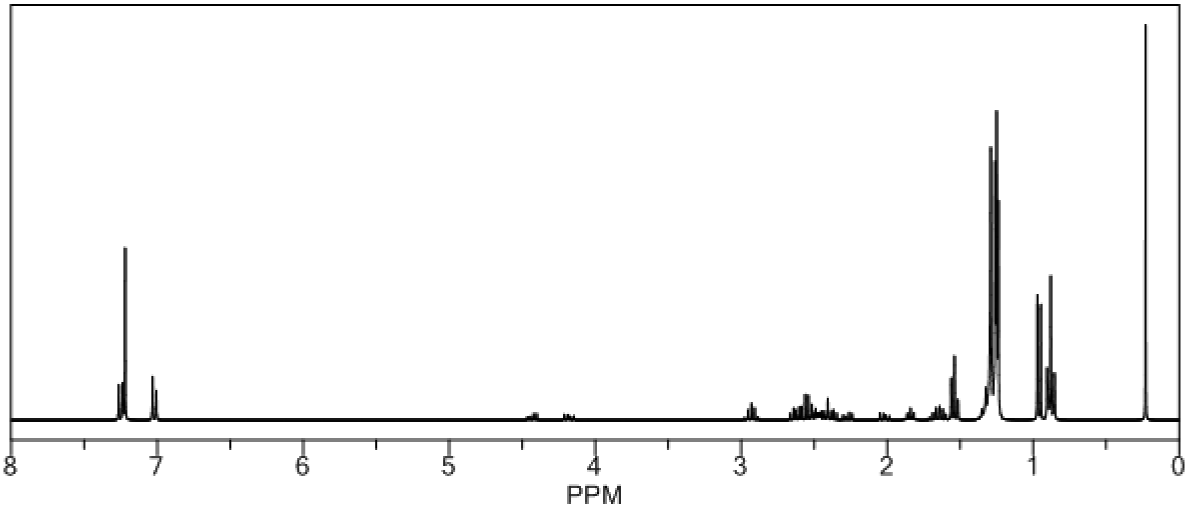


Figure 5. ^{1}H-NMR spectrum of the B_1 terpolymer

Conclusion

A green approach for synthesizing eleven miktoarm star terpolymers based on (Jojoba: DVB: alkylacrylate) and (jojoba: DVB: α-olefin) was performed easily (one step reaction), via free radical polymerization using benzoyl peroxide as an initiator, and DVB as tetra-functional cross-linker. The prepared star terpolymers were characterized using GPC/SEC for determination of Mn, Mw, and PDI. The morphological structure was characterized using SEM. Thermal analysis for the prepared star polymers were done, and it was found that they exhibit good thermal stability properties. Star polymers structural characterization was performed by FT-IR and ^{1}H-NMR.

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References

[1] Schaefgren JR, Flory PJ. J. Am. Chem. Soc.,1948; 70: 2709.
[2] Decker D, Rempp P. C. R. Acad. Sci.,1965; 261: 1977.
[3] Zilliox J-G, Decker D, Rempp P. C. R. Acad. Sci., 1966; 262: 726.
[4] Zilliox J-G, Rempp P, Parrod J. J. Polym. Sci. (Part C), 1968; 22: 145.
[5] Ishizu K, Kitano H, Ono T, Uchida S. Polymer, 1999; 40: 3229–3232.
[6] Hadjichristidis N. J. Polym. Sci., Part A: Polym. Chem., 1999; 37: 857-871.
[7] Hadjichristidis, N, Iatrou H, Pitsikalis M, Mays J. Prog. Polym. Sci., 2006; 31: 1068-1132.
[8] Khanna K, Varshney S, Kakkar A. Polym. Chem., 2010; 1: 1171-1185.
[9] Higashihara T, Hayashi M, Hirao A. Prog. Polym. Sci., 2011; 36: 323-375.
[10] Altintas O, Vogt AP, Barner-Kowollik C, Tunca U. Polymer Chemistry, 2011; 3: 34-45.
[11] Iatridi Z, Tsitsilianis C. Polymers, 2011; 3: 1911-1933.
[12] Breiner U, Krappe U, Stadler R. Macromol. Rapid Commun., 1996; 17: 567-575.
[13] Suzuki J, Furuya M, Iinuma M, Takano A, Matsushita Y. J. Polymer Sci., Part B: Polym. Phys., 2002; 40: 1135-1141.
[14] Erhardt R, Zhang M, Böker A, Zettl H, Abetz C, Frederik P, Krausch G, Abetz V, Müller AHE. J. Am. Chem. Soc., 2003; 125: 3260-3267.
[15] Fukushima S, Miyata K, Nishiyama N, Kanayama N, Yamasaki Y, Kataoka K. J. Am. Chem. Soc., 2005; 127: 2810-2811.
[16] Sperschneider A, Schacher F, Gawenda M, Tsarkova L, Müller AHE, Ulbricht M, Krausch G, Köhler J. Small, 2007; 3: 1056-1063.
[17] Docampo P, Stefik M, Guldin S, Gunning R, Yufa NA, Cai N, Wang P, Steiner U, Wiesner U, Snaith HJ. Adv. Energy Mater., 2012; 2: 676-682.

[18] Hanisch A. Synthesis and self-assembly of novel ABC miktoarm star terpolymers, Ph.D. Dissertation, Bayreuth university, 2013.

[19] Nassar AM, Nasser RM, Khattab AF, and Abdel Azim AAA. Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil. Petroleum Science and Technology, 2008; 26: 1390-1402.

[20] Ahmed NS, Nassar AM, Nasser RM, Khattab AF, and Abdel- Azim AA. Synthesis and Evaluation of Some Polymers as Lubricating Oil Additives. Journal of Dispersion Science and Technology, 2012; 33: 668-675.

[21] Ahmed NS, Nassar AM, Nasser RM, Raouf MEA, and El-Kafrawy AF. Novel Terpolymers as pour point depressants and viscosity modifiers for lube oil. Journal of Petroleum Science and Technology, 2014; 32: 680-687.

[22] Ahmed NS, Nassar AM, Nasser RM, Raouf MEA and El-Kafrawy AF. The rheological properties of lube oil with terpolymeric additives. Journal of Petroleum Science and Technology, 2014; 32(17): 2115 – 2122.

[23] Nasser RM. The Behavior of Some Acrylate Copolymers As Lubricating Oil Additives. OmniScriptum GmbH &Co.KG, Germany, ISBN:978-3-659-31639-5, (2015).

[24] Nasser RM. Synthesis and Evaluation of Some Lubricating Oil Viscosity Index Improvers and Pour Point Depressants. OmniScriptum GmbH &Co.KG, Germany, ISBN:978-3-330-33270-6, (2017).

[25] Cheremisinoff NP. Polymer Characterization Laboratory Techniques and Analysis; Chapter 2, Noyes Publications, USA, 1996.

To whom correspondence should be addressed Dr. Rabab M. Nasser, Chemistry Department, University College of Samtah, Jazan University, Saudi Arabia and Egyptian Petroleum Research Institute, Department of Petroleum Applications, Nasr city, Cairo, Egypt, E: mail: rabab_nasser@yahoo.com