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Eyüp Özdemr[a]; Cengiz Soykan[a]; Mehmet Coşkun[a]; Misir A. Ahmedov[a]
[a] University of FIRAT, Faculty of Science and Arts, ELAZIG/TURKEY

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SYNTHESIS OF PHENACYLMETHACRYLATE: ITS CHARACTERIZATION AND POLYMERIZATION

Eyüp ÖZDEMİR, Cengiz SOYKAN, Mehmet COŞKUN,
Misir A. AHMEDOV

University of FIRAT, Faculty of Science and Arts, ELAZIĞ/TURKEY

Key words: Phenacylmethacrylate, poly (phenacylmethacrylate). Poly (Phenacylmethacrylate -Co-Styrene), Solubility parameter, Thermal analysis

ABSTRACT

Phenacylmethacrylate (PAMA), a new monomer containing two carbonyl groups (C=O), was obtained from phenacyl chloride and sodium methacrylate. The homopolymer of PAMA and its copolymer with styrene were prepared in dioxane by using benzoylperoxide (Bz_2O_2) as initiator. IR, ^{1}H-NMR and ^{13}C-NMR techniques were used to identify the structure of the monomer and polymers.The density of monomer, homopolymer and copolymer were found to be 1.13; 1.35 and 1.10 gr/ml respectively. Also, limit viscosity numbers, solubility parameters, glass transition and decomposition temperatures of polymers were determined.

INTRODUCTION

During the past 20 years, the synthesis of functional monomers, their polymerization and their use for the synthesis of new functional polymers have attracted considerable interest. Substitued styrenes A-Ph-CH=CH_2 (A=OCOMe); N-Acrylamides A-NH-CO-CH=CH_2 (A=C(Me_2)CH_2SO_3); N,N-Diacrylamides A-NR-CO-CH=CH_2 (R=Alkyl) and Vinylics/acrylics A-CH=CH_2 (A = CH_2OH) can be given as examples to these monomers (1). These monomers can be converted into homo and copolymers by using convenient techniques and some spectroscopic techniques for characterization can be used because of their functional groups (2, 3, 4).

Here we report a new monomer containing two carbonyl groups. And its physical properties. Its homopolymer and copolymer with styrene were prepared. These kinds of polymers have become increasingly important in applications for coatings, biological active materials (5, 6) and for the synthesis of a number of other speciality polymers (7).

EXPERIMENTAL

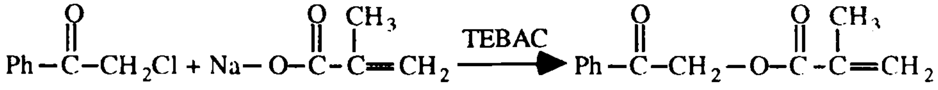
Purifications of materials

Reagents grade chemicals were dried on anhydrous magnesium sulphate and purified by distillation before use.

Synthesis of monomer

Phenacylmethacrylate (PAMA) $(Ph-\overset{O}{\overset{\|}{C}}-CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2)$ was synthesised by the reaction of phenacylchloride $(Ph-\overset{O}{\overset{\|}{C}}-CH_2Cl)$ and sodiummethacrylate $(Na-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2)$ by using triethylbenzylammonium chloride (TEBAC) (Aldrich) as a phase transfer catalyst better (8).

The reaction is:



$$Ph-\overset{O}{\overset{\|}{C}}-CH_2Cl+Na-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2\xrightarrow{TEBAC}Ph-\overset{O}{\overset{\|}{C}}-CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

Phenacylchloride and sodium methacrylate were prepared in our laboratory. For the synthesis of PAMA, 16.0 g of phenacylchloride, 17.6 g of sodium methacrylate and 2.2 g of TEBAC were put into a beaker of 250 ml. A small amount of hydroquinone was added to this mixture to inhibite the polymerization of PAMA. The mixture was stirred at 60°C for 36 hours. PAMA was extracted with diethylether and was dried over magnesium sulphate. Ether was evaporated and PAMA was distilled under vacuum (b.p. = 152°C at 3 mmHg., 13.8 g monomer was obtained, the yield is 65 %). FT-IR (cm-1): 3040 (= C-H, aromatic), 2980-2840 (C-H, alifatic), 1725 (-C=O-, ester), 1690 (-C=O-, attached to aromatic ring), 1630 (C=C), 1600 and 1580 (C = C, aromatic).

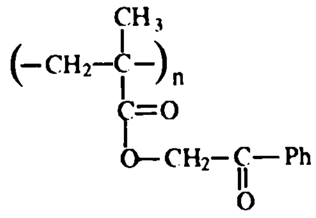
Polymerization of PAMA

PAMA was freed from inhibitor by washing with 5% KOH solution followed by distilled water, drying over anhydrous $MgSO_4$ and distillation under vacuum. 0.01 g of Bz_2O_2 using as initiator was dissolved in 1 ml dioxane. 1.00 g of PAMA, 1 ml Bz_2O_2 solution in dioxane and 5 ml pure dioxane were mixed in a reaction tube. After the sealed tubes had been kept at 60°C for 36 hours, the contents of tube were poured into 50 ml ethanol- 70 ml water mixture. Poly (PAMA) was purified by repeated precipitations by ethanol and finally dried under vacuum.

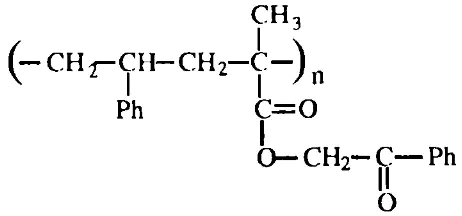
Copolymerization of PAMA with Styrene

0.7 g of PAMA, 0.3 g of styrene, 1 ml Bz_2O_2 (0.1 %) solution in dioxane and 4 ml pure dioxane were mixed in a reaction tube at 60°C for 36 hours. Poly (PAMA-Co-St) was precipitated by ethanol and dried under vacuum. Chemical structures of Poly (PAMA) and Poly (PAMA-Co-St) are given as following:

Poly (PAMA) :



Poly (PAMA-Co-St):



$$\left(-CH_2-\underset{Ph}{CH}-CH_2-\overset{CH_3}{\underset{C(=O)-O-CH_2-C(=O)-Ph}{C}}-\right)_n$$

Instrumentation

I.r. spectra of the monomer, its homopolymer and copolymer were recorded with a PYE UNICAM SP3 -100 i.r. spectrophotometer. ^1H -NMR and ^{13}C-NMR spectra of monomer and polymer were taken with a GEMINI 200 MHz nuclear magnetic resonance spectrometer and thermogravimetric analysis were performed with a Shimadzu thermal analyser system.

RESULTS AND DISCUSSION

The I.R. spectra of monomer PAMA, poly (PAMA) and its copolymer Poly (PAMA-Co-St) are shown in Fig. 1.

If a comparision is made among the i.r. spectra of PAMA with those of poly (PAMA) and Poly (PAMA-Co-St), we will see that the spectra of polymers haven't given a band at 1630 cm^{-1} which is a characteristics for the monomer. In addition, since α, β unsaturation to -C=O- in the monomer during the polymerization disappeared, the carbonyl absorption shifted from 1725 cm^{-1} to 1740 cm^{-1}.

^1H-NMR spectra of PAMA , and poly (PAMA), and Poly (PAMA-Co-St) were taken using $CDCl_3$ as solvent. These spectra are shown in Fig 2.

^{13}C-NMR spectrum of the monomer is shown in Fig 3. The ester and keto carbonyls of PAMA gave signals at 168 ppm and 193 ppm respectively. Quaternary carbon of phenyl ring gave a less intense peak at 135 ppm and meta, ortho and para carbons of the phenyl ring gave more intense peaks at 128, 129 and 134 ppm respectively. Peaks at 136 ppm for C=, at 127 ppm for = CH_2, at 66 ppm for -OCH_2 and at 19 ppm for -CH_3 are the other characteristics.

^{1}H-NMR spectrum of poly (PAMA) shows signals at 7.2 -7.6 ppm for meta and para protons, and signal at 7.6-8.0 ppm for ortho protons in aromatic ring, at 5.2-5.8 ppm for methylene protons of phenacyl group, at 1.0-2.6 ppm for methylene protons in polymer chain and methyl protons an polymer chain. The phenyl ring protons of styrene and PAMA units in the copolymer were appeared at 6.6 - 6.7 ppm and 7.3 - 7.8 ppm respectively as can be seen in the Fig 2. Protons of -CH_2-O-CO- in PAMA unit and protons of methine, methylene and methyl groups in all copolymer chain were seen as broad signals at 4.0 - 5.2 ppm and 0.4 - 2.8 ppm respectively.

Physical parameters

Some physical parameters like densities (δ) of monomer and polymers, molar refractive index $(R_L)_D$ of monomer, solubility parameters (δ) of polymers at 20°C and limit viscosity numbers $[\eta]$ of polymers at 25°C were determined in the study. The density of the monomer was determined by using a pycnometer whereas the densities of polymers were found by applying floating method (9). Lorentz-Lorenz equation was used to calculate the molar refractive index after reading the specific refractive index of the monomer from the refractometer (10). The limit viscosity numbers of poly (PAMA) and Poly (PAMA-Co-St) were determined in dioxane, and also the solubility parameter of homo and copolymer were determined by using titration method (11). These values are shown in Table 1.

As expected, the density of homopolymer is higher than that of monomer. $(R_L)_D$ value was also found to be 53.70 cm^3 by summing atom, structure and attraction values of monomer (12). $(R_L)_D$ value was found to be 53.67 cm^3 by Lorenz and Lorentz formula (10). Two values of $(R_L)_D$ show aggreement with each other.

Table 1. Some physical parameters of monomer and polymers

Compound	d (gr/cm^3)	$(R_L)_D$ (cm^3)	δ (cal/cm^3)$^{1/2}$	[η] (dl/gr)
PAMA	1.13	53.66	-----	-----
poly (PAMA)	1.35	-----	9.90	0.81
Poly (PAMA-Co-St)	1.10	-----	10.20	1.13

Thermal Analysis

Thermal analysis curves of poly (PAMA) and Poly (PAMA-Co-St) are shown in Figs 4 and 5. The glass transition temperatures (Fig. 4) both homo and copolymer were found to be 105°C approximately. This means that the styrene unit hasn't changed the T_g value of poly (PAMA). The homopolymer underwent decomposition in two stages (Fig. 5). The first Fig. 5 stage was observed at 207-300°C and weight loss was about 67 % in this region. The second stage decomposition became at 300-430°C with weight loss of 32.5 %. The degradation of the copolymer occured at 248-430°C in a single stage (Fig. 5). The residue was lower than 1 % for the both homopolymer and copolymer. Lower decomposition rate after 300°C in the homopolymer degradation and degradation with a single stage of copolymer may be evidence of intermolecular reactions between side groups in neighbour units of homopolymer. Since PAMA units were disconnected by styrene units, the reactions mentioned above may not occure in the copolymer.

CONCLUSION

The preparation of PAMA and its homopolymer and copolymer with styrene were considered in this work. The monomer and its homo and copolymer with styrene were identified with i.r., ^{1}H-NMR and ^{13}C-NMR techniques and also some of the physical parameters of the compounds were determined. The glass transition and thermal degradation temperatures of the polymers were found by using thermal analysis.

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