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Mild Synthesis, Characterization, and Application of some Polythioester Polymers Catalyzed by Cetrimide Ionic Liquid as a Green and Eco-Friendly Phase-Transfer Catalyst

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ABSTRACT

In this research, we develop and prepare some of the polymers based on polythioesters using cetrimide as an ionic liquid and phase transfer catalyst. All of the polymers were prepared through the reaction of 5,5'-methylenebis (1,3,4-oxadiazole-2-thiol) with five types of diacyl chloride derivatives in the presence of cetrimide as phase transfer catalyst in the mixture of water and chloroform at room temperature. The chemical structure of synthesized polymers was determined using ^{1}H NMR and ^{13}C NMR spectroscopy. The mechanical and thermal stability of the synthesized polymers were investigated. In addition, using DFT calculation, the chemical optimization of synthesized polymers was presented. Moreover, the catalytic activity of cetrimide was compared with four types of ionic liquid with phase transfer catalyst roles. Additionally, the application of synthesized polymers in bone cement was investigated.

Keywords: *Polymer, ionic liquid, phase transfer catalyst, polythioesters, bone cement, cetrimide*

1. Introduction

The presence of sulfur atoms on different polymers is an interesting field of research, especially in the synthesis of pharmaceutical drug carriers based on polythioesters [1-3]. The introduction of sulfur atoms on the main backbone of polymers could be increased the optical, thermal, mechanical, electronical, and chemical resistance of polythioesters [4-6]. Nowadays, different polymers containing sulfur atoms such as polythiocarbonates, polythiourethanes, polythioesters, polysulfur-random-styrene, and polythioethers, have been produced [7-12]. Some of the polythioesters, such as polythioethyleneterphthalate are among the most widely produced polymers due to their high excellent resistance [13]. The pointed properties and other excellent properties such as low cost, allow them to be applied widely to provide films, fibers, and bone cement [14, 15]. In 1951, Marvel and co-workers described the first synthesis of polythiesters using the reaction of aliphatic dithiols and dibasic acid chlorides [16]. Then, Colleagues and Podkoscielny provided polythioesters using a polycondensation reaction. In this paper, diacyl chlorides were dissolved in an organic solvent such as benzene, hexane, or chloroform and then reacted with a series of dithiols [17, 18]. In addition, Sasanuma and co-workers described a new method for the synthesis of polythioesters using the reaction of dibromoalkanes and tetrathioterphthalic acid [19, 20]. The odor limitation of the use of thiols and thiocarboxylic acids in the synthesis of polythioesters is one of the important issues in this field. The biosynthesis of polythioesters is a great and interesting approach to dissolving this problem. In addition, aliphatic polythioesters are an important and interesting class of polymers with wide applications in different fields such as artificial tissues, drug delivery systems, and medical applications. Previously, for the production of polythioesters, the polycondensation of mercaptoacetic acid (thioglycolic acid) was used [14, 21]. However, this approach is requiring high-temperature reactions, and harmful wastewater, and is energy intensive. Due to the limitation of diverse of

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monomers, a limited range of polymers based on polythioesters could be synthesized. Therefore, the development of an efficient method for the preparation of polythioester polymers is highly desirable for different applications.

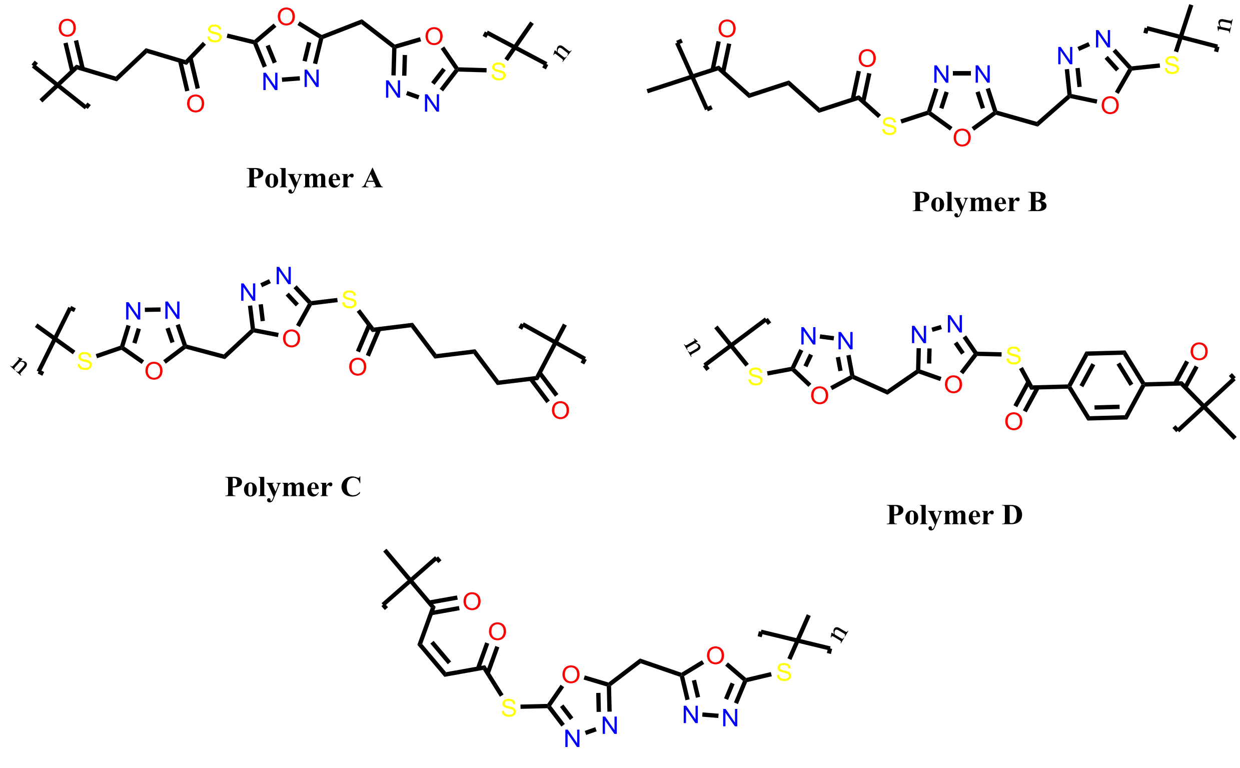
A phase transfer catalyst (PTC) is a catalyst that the migration of reactants and substrates facilitates from one phase into another phase where the reaction occurs. Alkyltrimethylammonium bromide or cetrimide is a mixture of dodecyltrimethylammonium, hexadecyltrimethylammonium, and tetradecyltrimethylammonium bromide (mixture of three quaternary ammonium compounds). These ammonium salts can perform a dual role including a phase transfer catalyst and an ionic liquid as solvent. In addition, the technology of phase transfer catalyst could speed up the process of reaction under mild reaction conditions [22-24]. Herein, we develop a new approach and method for the highly efficient and clean synthesis of polymers based on polythioesters with a different main backbone structure (**Fig. 1**) using cetrimide as an eco-friendly and green phase transfer catalyst.

2. Experimental

As you can see in **Scheme 1**, the synthesized polythioester polymers were prepared in five steps. First, dicarboxylic acids were converted to diacyl chloride derivatives. Next, the malonohydrazide was produced using the reaction of hydrazine in ethanol as the organic solvent. Then, the 5,5'-methylenebis(1,3,4-oxadiazole-2-thiol) was provided as a key intermediate for the synthesis of polymers A-E.

Synthesis of diacyl chloride derivatives using dicarboxylic acids (2a-2e)

The dicarboxylic acid chloride monomers were prepared and used immediately and directly under dry conditions by refluxing the thionyl chloride with the dicarboxylic acids, where (50 mmol) of the dicarboxylic acids were placed in the reaction flask, followed by the addition of (15 mL) of thionyl chloride slowly with cooling under conditions Dry, followed by reflux of the reaction components at 70 ºC until the complete dissolution of the dicarboxylic acids and making sure that no gases emitted (HCl and SO_2), to obtain a white precipitate of terephthaloyl chloride (2a), and products colorless liquid for each of succinoyl (2c), glutaryl (2d), edipoyl (2e) and maleyl chloride (2b).


Polymer A

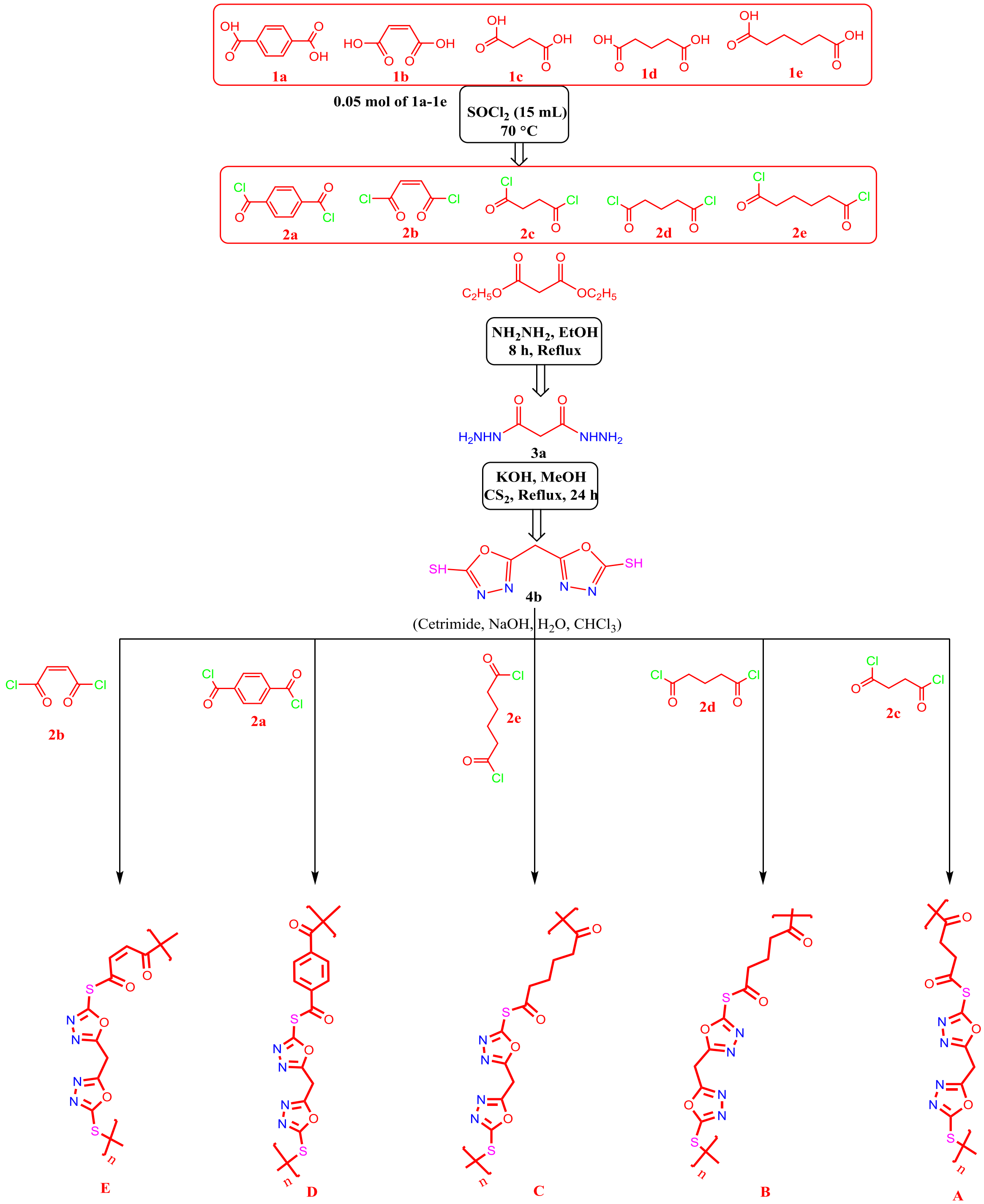
Polymer B

Polymer C

Polymer D

Polymer E

Fig. 1. The chemical structure of synthesized polythioesters polymers



Scheme 1. Synthesis of five types of polythioester polymers using cetrimide as an ionic liquid phase transfer catalyst

Synthesis of malonohydrazide (3a)

A mixture of diethyl malonate (0.1 mol) and (50 mL) of 80% hydrazine hydrate in 150 mL ethanol, was heated under reflux conditions for 12 hours. After completion of the reaction (monitored by TLC- n-hexan: EtOAc (7:2)), the solution was concentrated under vacuum pressure. The formed precipitate was filtered and recrystallized from ethanol, to give a white precipitate with a melting point of 150-154 °C and a yield of 85% (3a).

Synthesis of 5,5'-methylenebis(1,3,4-oxadiazole-2-thiol) (4b)

To a mixture of malonohydrazide (3a) (0.1 mol) in an alcoholic solution of potassium hydroxide (0.4 mol of potassium hydroxide dissolved in 150 mL of ethanol), Followed by the slow addition of 50 mL of CS$_2$ to the reaction mixture under dry conditions. The reaction mixture was refluxed until the hydrogen sulfide gas was no longer emitted. The progress of the reaction was monitored by TLC (n-hexan: EtOAc) (7:2) or petroleum ether: EtOAc (8:2). After the reaction was completed, the solvent was completely removed and the remainder was poured into water and acidified with concentrated hydrochloric acid. The formed precipitate was filtered, dried, and recrystallized from ethanol, to give a yellow precipitate that decomposes at a temperature higher than 300 °C with a yield of 80% (4b).

Synthesis of five types of polythioester polymers (A-E) using cetrimide as an ionic liquid phase transfer catalyst

Diacyl chloride derivatives (2a-2e) and synthesis of 5,5'-methylenebis(1,3,4-oxadiazole-2-thiol) (4b) was polymerized using interfacial poly-condensation with chloroform–water interphase system and cetrimide as phase transfer catalyst. In a round bottom flask, a mixture of 0.01 mol of sodium hydroxide dissolved in 10 mL of water with 0.005 mol of synthesis of 5,5'-methylenebis(1,3,4-oxadiazole-2-thiol) (4b), 10 mg of cetrimide (phase transfer catalyst) dissolved in 5 mL of water was added. The organic phase was prepared by dissolving 0.005 mol of diacylchloride monomers (2a-2e) in 20 mL of chloroform, the organic phase was added to the water phase rapidly and mixed at room temperature with a stirrer for 5 min. Then, 20 mL of acetone was added. The polymers were separated by filtration and washed with acetone and distilled water to the removed unreacted starting material and second product such as sodium chloride. The products were dried in the oven at 60 °C for 1 h.

Names and physical data of applied monomers and polythioesters

*Terephthaloyl dichloride (**2a**), Chemical Formula: $C_8H_4Cl_2O_2$, Exact Mass: 201.95883, Molecular Weight: 203.01800, m/z: 201.95883 (100.0%), 203.95588 (63.9%), 205.95293 (10.2%), 202.96219 (8.7%), 204.95924 (5.5%).*

*Maleoyl dichloride (**2b**), Chemical Formula: $C_4H_2Cl_2O_2$, Exact Mass: 151.94318, Molecular Weight: 152.95800, m/z: 151.94318 (100.0%), 153.94023 (63.9%), 155.93728 (10.2%), 152.94654 (4.3%), 154.94359 (2.8%), Elemental Analysis: C, 31.41; H, 1.32; Found: C, 30.89; H, 1.25.*

*Succinyl dichloride (**2c**), Chemical Formula: $C_4H_4Cl_2O_2$, Exact Mass: 153.95883, Molecular Weight: 154.97400, m/z: 153.95883 (100.0%), 155.95588 (63.9%), 157.95293 (10.2%), 154.96219 (4.3%), 156.95924 (2.8%).*

*Glutaroyl dichloride (**2d**), Chemical Formula: $C_5H_6Cl_2O_2$, Exact Mass: 167.97448, Molecular Weight: 169.00100, m/z: 167.97448 (100.0%), 169.97153 (63.9%), 171.96858 (10.2%), 168.97784 (5.4%), 170.97489 (3.5%).*

*Adipoyl dichloride (**2e**), Chemical Formula: $C_6H_8Cl_2O_2$, Exact Mass: 181.99013, Molecular Weight: 183.02800, m/z: 181.99013 (100.0%), 183.98718 (63.9%), 185.98423 (10.2%), 182.99349 (6.5%), 184.99054 (4.1%).*

*Malonohydrazide (**3a**), Chemical Formula: $C_3H_8N_4O_2$, Exact Mass: 132.06473, Molecular Weight: 132.12300, m/z: 132.06473 (100.0%), 133.06808 (3.2%), 133.06176 (1.5%), Elemental Analysis: C, 27.27; H, 6.10; N, 42.41; Found: C, 26.89, H, 5.69, N, 41.89.*

*5,5'-methylenebis(1,3,4-oxadiazole-2-thiol) (**4b**), Chemical Formula: $C_5H_4N_4O_2S_2$, Exact Mass: 215.97757, Molecular Weight: 216.23300, m/z: 215.97757 (100.0%), 217.97336 (9.0%), 216.98092 (5.4%), 216.97695 (1.6%), 216.97460 (1.5%), Elemental Analysis: C, 27.77; H, 1.86; N, 25.91; S, 29.65, Found C, 26.58, H, 1.75, N, 24.78, S, 28.89.*

*S-(5-((5-(mercapto)-1,3,4-oxadiazol-2-yl)methyl)-1,3,4-oxadiazol-2-yl)-4-oxobutanthioate (**Polymer A**), M. P.: 257 ℃ decompose, Color: red-brown, IR (υ cm^{-1}): 3211, 3023, 2989, 2968, 1654, 1245, 1156, 1025, 1023, 989, 897, 758, 965, 654.*

*S-(5-((5-(mercapto)-1,3,4-oxadiazol-2-yl)methyl)-1,3,4-oxadiazol-2-yl)-5-oxopentanethioate (**Polymer B**), M. P.: 191-193 ℃, Color: reddish brown, IR (υ cm^{-1}): 3125, 3026, 2969, 2935, 1789, 1654, 1245, 1156, 1025, 1019, 989, 897, 758, 965, 654.*

*S-(5-((5-(mercapto)-1,3,4-oxadiazol-2-yl)methyl)-1,3,4-oxadiazol-2-yl)-6-oxohexanethioate (**Polymer C**), M. P.: 169-172 ℃, Color: turmeric, IR (υ cm^{-1}): 3011, 3003, 2989, 2968, 1654, 1246, 1156, 1025, 1023, 989, 896, 758, 965, 626.*

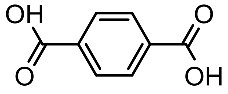
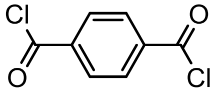
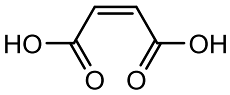
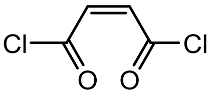
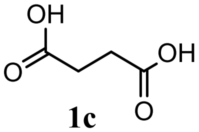
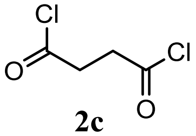
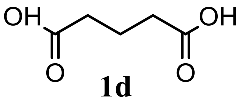
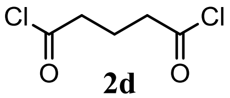
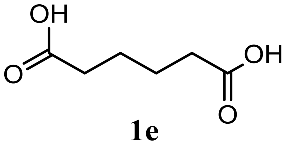
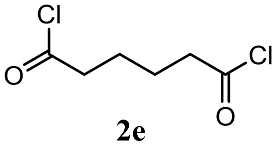
*S-(5-((5-mercapto-1,3,4-oxadiazol-2-yl)methyl)-1,3,4-oxadiazol-2-yl)4-formylbenzothioate (**Polymer D**), M. P.: >350 ℃ decompose, Color: orange, IR (υ cm^{-1}): 3078, 3033, 2954, 2948, 1754, 1246, 1158, 1085, 1028, 969, 896, 758, 965, 568.*

*S-(5-((5-(mercapto-1,3,4-oxadiazol-2-yl)methyl)-1,3,4-oxadiazol-2-yl)(Z)-4-oxobut-2-enethioate (**Polymer E**),* *M. P.: >350 ℃ decompose, Color: pale orange. IR (ν cm^{-1}): 3257, 3123, 2968, 2936, 1654, 1458, 1246, 1158, 1055, 1018, 989, 896, 758, 965, 566.*

3. Results and Discussion

The diacyl chloride derivatives were prepared from the reaction of terphthalic acid (1a), maleic acid (1b), succinic acid (1c), glutaric acid (1d), and adipic acid (1e) and thionyl chloride at 70 °C under reflux conditions. This method is a well-known and efficient approach for the synthesis of acyl chloride derivatives [25-27]. The results of the above reactions were shown in **Tables 1** and **2**. Some of the organic reactions are simply carried out under homogeneous reaction conditions, while not under heterogeneous reaction conditions. In addition, many organic reactions are incomplete in the two-phase of water and organic solvent. Although the stirring of the reaction mixture can increase the chance of mutual components of the reaction, the effect is not very clear and obvious [28]. In the current research, cetrimide as quaternary ammonium salt was selected in order to obtain good lipophilicity and good hydrophillicity. In the pointed phase transfer catalyst (cetrimide), the higher symmetry of the ammonium salt cause shielded the positive charge and led to the better catalytic activity of the phase transfer catalyst [29, 30]. In order to obtain the optimum reaction conditions for the use of a phase transfer catalyst, the catalytic activity of cetrimide was investigated by many factors including catalytic amount, solvent type, stirring speed, type of base, and temperature. These factors were checked in the synthesis of polymer A as a model reaction (**Table 3**). All of the organic reactions need to investigate the effect of solvent on the yield and kinetic of the reaction. Different organic solvents including CH_2Cl_2, $CHCl_3$, CH_3CN, and DMF were considered as organic solvent in the mixture with water (**Table 3**, entries 1-4). The obtained results showed that $CHCl_3$ was the best solvent for this reaction. In the presence of phase transfer catalyst, the size of interface area would be controlled by stirring rate in the reaction mixture. By increasing the stirring speed, the molecular collision would be increased during the reaction. By increasing the stirring speed to 300 rpm.min-1 the yield of reaction was increased (**Table 3**, entry 5). In addition, sodium hydroxide showed the best efficiency in this reaction relative to KOH, and Na_2CO_3 (**Table 3**, entries 7 and 8). Also, the effect of the catalytic amount of cetrimide and the temperature of the reaction was monitored in the model reaction (**Table 3**, entries 9-11).

Table 1. Synthesis of diacyl chloride (2a-2e) using thionyl chloride

Entry	Dicarboxylic acid	Diacyl chloride	Conversion (%)^b	Yield (%)^c
1	 **1a**	 **2a**	96	86
2	 **1b**	 **2b**	95	89
3	 **1c**	 **2c**	91	90
4	 **1d**	 **2d**	95	93
5	 **1e**	 **2e**	97	93

a) Reaction conditions: 1a-1e (50 mmol), $SOCl_2$: 15 mL, T: 70 °C, Time: 6 h.

b) and c) Based on the GC chromatogram, in this part the area of the peak of the pointed product or substrate was calculated and then applied in the following formula $(R_u/R_s)*(C_s/C_u)*$Standard purity

Table 2. Synthesis of compounds 3b and 4b

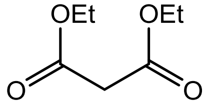
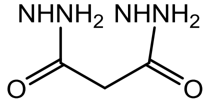
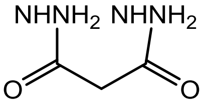
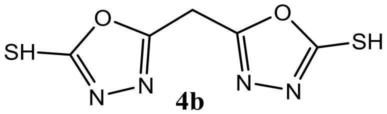
Entry	Starting Material	Product	Yield (%)	M. P. (°C)
1	 **2b**	 **3b**	97	148-152 (Yellowish-white)
2	 **3b**	 **4b**	98	>350 °C decompose (Yellowish-white)

Table 3. Optimization reaction conditions for the synthesis of polymer A using cetrimide[a]

Entry	Organic Solvent	Stirring speed (rpm.min^{-1})	Type of base	Amount (mg)	T (°C)	Yield (%)[b]
1	CH_2Cl_2	200	KOH	10	25	69
2	$CHCl_3$	200	KOH	10	25	75
3	CH_3CN	200	KOH	10	25	50
4	DMF	200	KOH	10	25	46
5	$CHCl_3$	300	KOH	10	25	77
6	$CHCl_3$	400	KOH	10	25	77
7	$CHCl_3$	300	NaOH	10	25	91
8	$CHCl_3$	300	Na_2CO_3	10	25	30
9	$CHCl_3$	300	NaOH	5	25	60
10	$CHCl_3$	300	NaOH	15	25	85
11	$CHCl_3$	300	NaOH	10	40	70

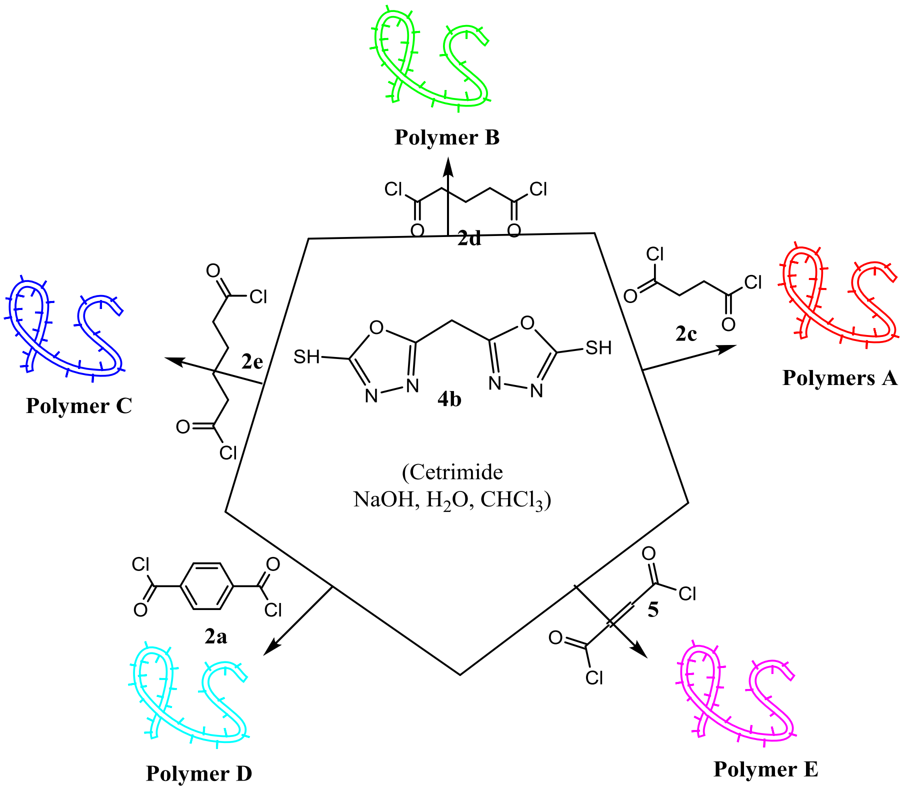
a) Reaction conditions: 0.005 mol of 2c, 0.005 mol of 4b, base: 0.01 mol, water: 10 mL, b) Isolated yield.

After the preparation of 5,5'-methylenebis(1,3,4-oxadiazole-2-thiol) (4b) and with optimization reaction conditions in hands, we decided that a series of polythioester synthesized and characterized. Hence, the compound (4b) was reacted with some synthesized diacyl chloride in the presence of cetrimide as a phase transfer catalyst (**Scheme 2**). According to **Scheme 2**, all of the used acyl chlorides readily reacted with the compound (4b) in good to excellent yields to produce polymer A to E with 91%, 94%, 89%, 86%, and 94%, respectively.

After the preparation of polymers A-E (^{1}H NMR and ^{13}C NMR spectra of polymers were provided in supporting information), the thermal stability of prepared polythioesters was considered (**Fig. 2**). The thermal properties of polythioester polymers A-E were studied by thermogravimetric analysis (TGA). As can be seen, the TGA thermograms indicated that the temperature of decomposition for polymers A, B, C, D, and E were 257, 193, 172, 325, and 349 °C, respectively at 10% weight loss of water. Also, the DSC data show that the glass transition temperature of synthesized polymers A, B, C, D, and E were measured at 89, 91, 67, 97, and 98 °C, respectively. In addition, single-step degradation was observed in all of the synthesized polythioesters. As can be seen, the temperature of decomposition in all of the polymers was higher than in the pure monomers.

The limiting oxygen index or (LOI) is a character of polymers that indicates the percentage of oxygen to be present to support the polymers. As we know, the percentage of oxygen in the air is approximately 21% and it is obvious that all compounds with LOI lower than 21% will burn simply, while other compounds with a higher LOI will tend not to burn. In addition, the char residue (CR) of polymers could be calculated as criteria for the evaluation of the LOI of polymers. It is notable that there is a linear relationship between CR and LOI for hydrogen-free polymers according to Van Krevelen (Eq. 1) [31-33].

$$\text{LOI}=\frac{(17.5+0.4\,CR)}{100} \quad \text{Eq. (1)}$$



Scheme 2. Rapid synthesis of some polythioester polymers using cetrimide as an ionic liquid and phase transfer catalyst

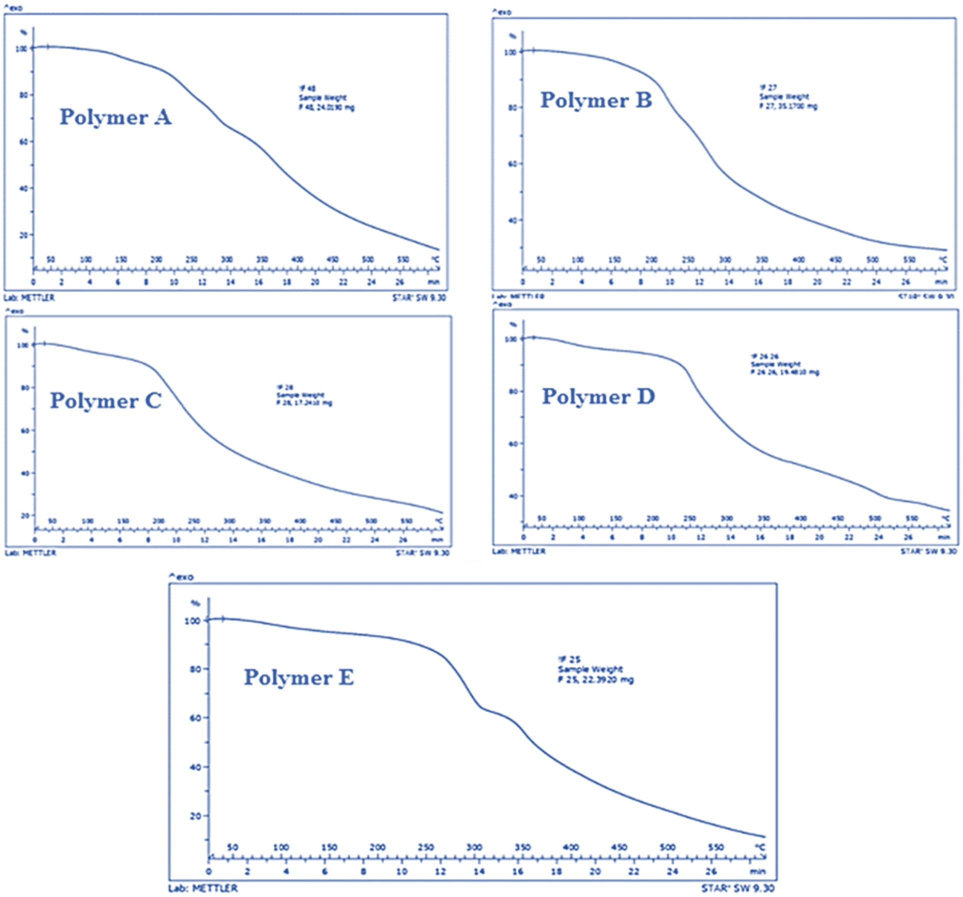


Fig. 2. TGA spectra of polythioesters polymers in the presence of cetrimonium bromide as phase transfer catalyst

In accordance with Eq. (1), a higher CR yield will increase flame retardance. The values of LOI for polymers A-E including 5%, 10%, and 15% were 28.4, 34.6, 37.1, 38.9, and 40.2, respectively. In addition, the heat of combustion (ΔH_{comb}. j.g^{-1}) for polymers could be calculated from the Eq. (2).

$$LOI=\frac{8000}{\Delta H\ com}$$

According to Eq. (2), the ΔH_{comb} was 281.7, 231.2, 215.6, 205.6, and 199.0 Kj.g^{-1}, for polymers A-E, respectively. In addition, the mechanical properties of polymers A-E are shown in **Fig. 3**. The mechanical properties of polymers were increased by increasing CH_2 (methylene groups). Finally, in order to show the efficiency of cetrimonium bromide as a phase transfer catalyst, some of the ionic liquids with phase transfer catalyst roles were provided and used as the catalysts for the synthesis of polythioester polymers. The chemical structures of them are shown in **Fig. 4**. After preparation of ionic liquid phase transfer catalyst 1-4 (IL-PTC-1 to IL-PTC-4), the reaction of 1,3-bis(5-mercapto-1,3,4-oxadiazol-2-yl)propane-1,3-dione (4b) with compounds 2a, 2c-e, and 5 performed. The obtained results were shown in **Table 4**. As can be seen, the obtained results were clearly shown that the cetrimide act as a powerful phase transfer catalyst for the transformation of the different substrate between the organic and aqueous phase for the production of polymers. In addition, the optimized chemical structure of synthesized polythioesters using DFT calculation at the B3LYP/6-31G* level was measured. The optimized chemical structures were shown in **Fig 5**. It is notable that for ease of calculation, the two monomers in the chemical structure of polymers were used.

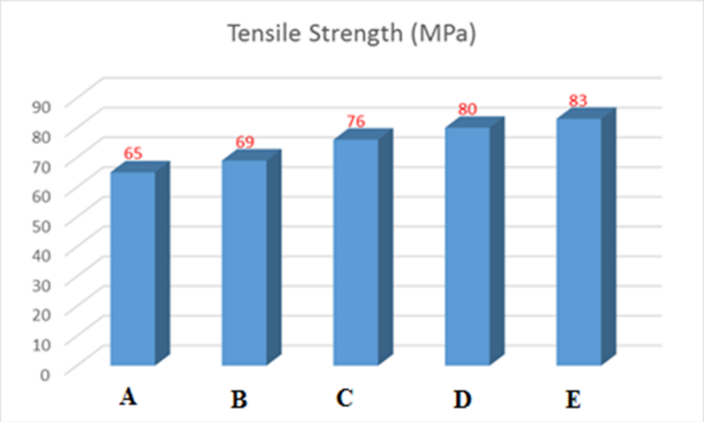


Fig. 3. The mechanical properties of Polymers A-E

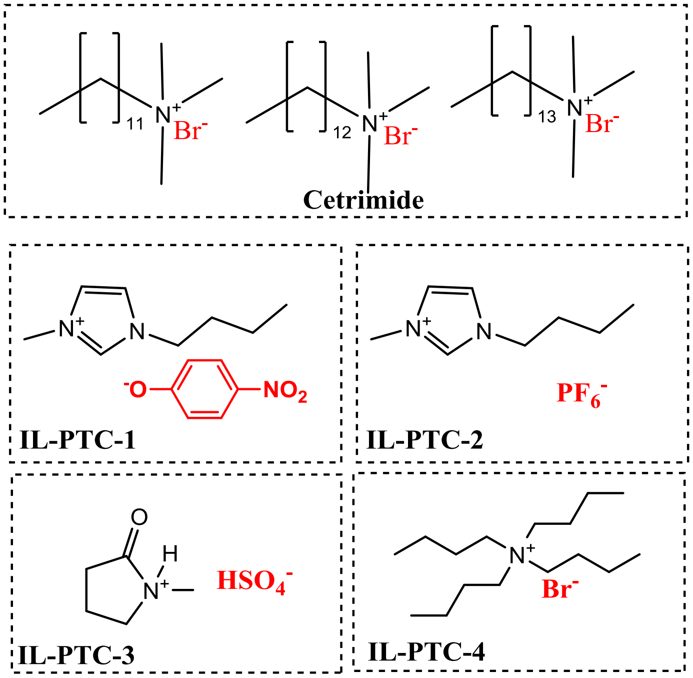


Fig. 4. The chemical structure of ionic liquid with phase transfer catalyst role

Table 4. The comparison of obtained results for the synthesis of polythioesters using different catalysts

	Polymer A	Polymer B	Polymer C	Polymer D	Polymer E
Cetrimide	91%	94%	89%	86%	94%
IL-PTC-1	N.F.	<20%	N.F.	N.F.	<20%
IL-PTC-2	40%	35%	50%	40%	45%
IL-PTC-3	N.F.	N.F.	N.F.	N.F.	N.F.
IL-PTC-4	65%	70%	75%	65%	60%

N. F. : Not Formed.

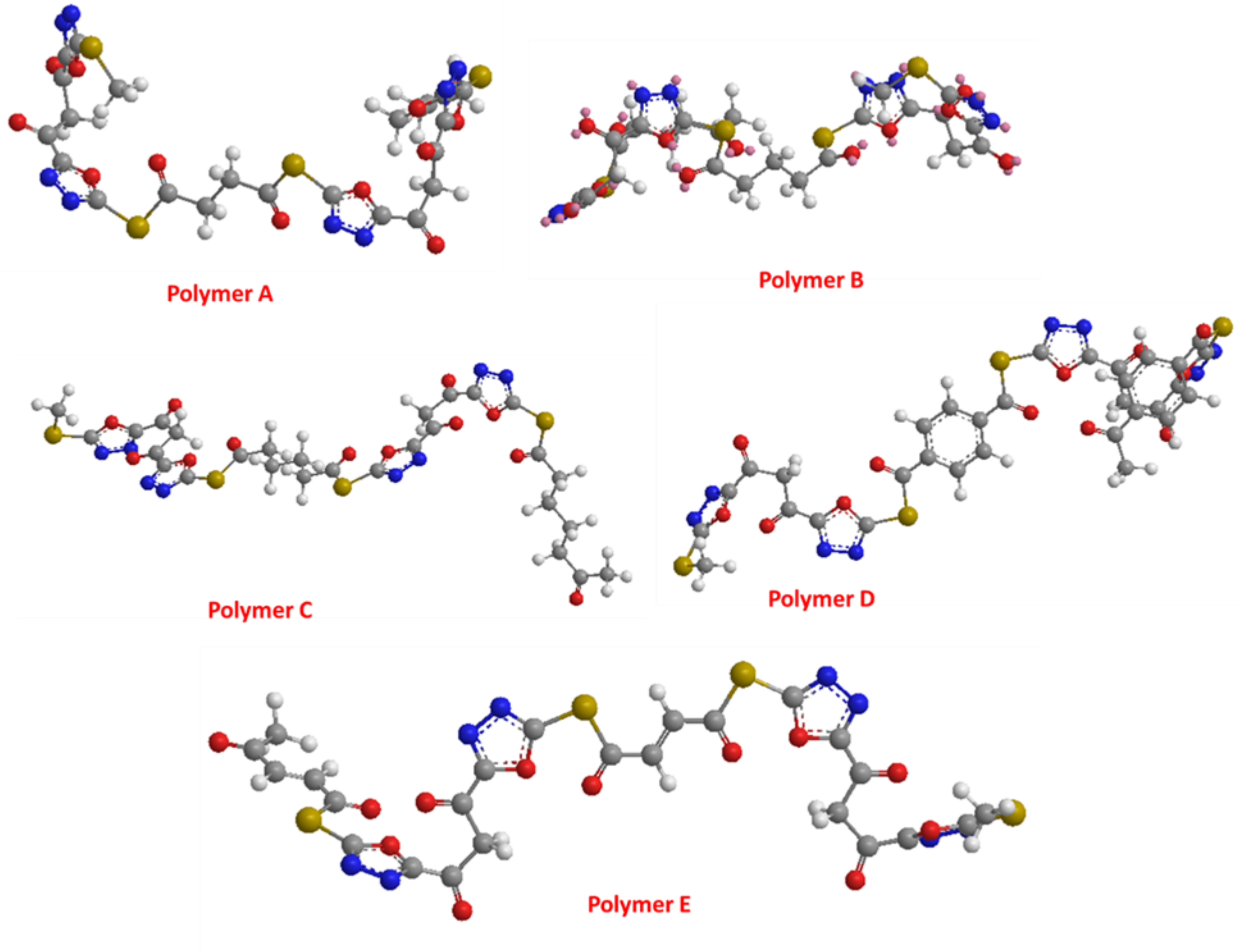


Fig. 5. The optimized chemical structure of polymers A-E using DFT calculation at the B3LYP/6-31G* level

After the successful preparation of polythioesters, we decided that the prepared polymers could be applied in different fields. Therefore, bone cement was selected for the application of synthesized polymers. As we know, proper fixation on the bone in the human body is an important issue for joint replacement. Up to now, several polymers were used in bone cement [34-38]. We observed that after the addition of the optimized amount of polymer C to bone cement, the mechanical tensile strength was increased (wt. 0.03%). Among the synthesized polymers, polymer C shows the best efficiency for the improvement of the mechanical properties of bone cement.

4. Conclusions

In summary, we prepared five types of polymers based on polythioesters using cetrimide as an ionic liquid and phase transfer catalyst. The chemical structure of synthesized polymers was determined using ^{1}H NMR and ^{13}C NMR spectroscopy. The mechanical and thermal stability of the synthesized polymers were investigated and showed good results. In addition, using DFT calculation, the chemical optimization of synthesized polymers was presented. Moreover, the catalytic activity of cetrimide was compared with four types of ionic liquid with phase transfer catalyst roles.

Additionally, the application of synthesized polymers in bone cement was investigated and polymer C shows good mechanical and thermal stability in bone cement.

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