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A Yield Study on Self-Initiated Photopolymerization of Acrylate Monomers Bearing Benzophenone Pendant Unit

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ABSTRACT: The objective of this study was to determine the photo-initiator potentials of the acrylate monomers, p-benzophenoneoxycarbonylphenyl acrylate (U1) and p-benzophenoneoxycarbonyl phenyl metacrylate (U2), having self-initiated photo-polymerization characteristic thanks to benzophenone groups presenting in their molecular structures. The effect of the co-initiator types (triethylamine, N-methyldiethanolamine and 4,N,N-trimethylanaline), the solvents used in the photo reactions (DMSO, EtOAc and acetone) and co-initiator concentration on the percent conversion of both monomers were investigated in details. The characterizations of the obtained polymer products were done by FTIR, ^{1}H-NMR and DSC techniques. Among co-initiators, the results revealed that the maximum percent conversion, 21.32 % was obtained from the photo-reaction carried out with TEA with the use of U1 monomer. Moreover, the obtained findings showed that the degree of monomer conversion increased with the increasing of the solvent polarity strength (DMSO>EtOAc>acetone). Correspondingly, the maxima, 22.54 % and 19.28 % were recorded with DMSO for both U1 and U2 monomers, respectively. Moreover, the percent conversion increased almost linearly with the increasing of the co-initiator concentration in the reaction medium. The maximum values were found to be 31.27 % and 26.10 % for U1 and U2 at 13.5x10^{-2} M triethylamine concentration, respectively. This was caused probably from the increment in the rate of polymerization reaction due to the formation of the relatively higher amount radicals during the photo-reaction.

Keywords – *Photo-polymerization, Percent conversion, Acrylate monomer, Benzophenone group, Self-initiation.*

1. Introduction

The photo-initiated free radical polymerization have been used commonly to prepare the advanced polymeric materials and attracted much attention due to large application areas such as adhesives, printing inks, photo-resists and curing of coatings etc.(Aydin, Temel, Balta, and Arsu, 2015). The most striking advantage of the photo-polymerization is that the polymerization is carried out at room temperature or below in contrast to thermally based polymerization requiring the elevated temperatures and the probability of occurring the side reactions such as chain transfer is fewer than the thermally induced polymerization (Yagci, Jockusch, and Turro, 2010). The initiation in the free radical photo-polymerizaton takes place in two ways by using α-cleavage (Type I) and H-abstraction (Type II) initiators (Akat, Ozkan, and Saltan, 2012; Allen et al., 1988; Tehfe et al., 2013). Common type II photo-initiators system contain the aromatic carbonyl groups such as benzophenone groups (Temel, Karaca, and Arsu, 2010; Wrzyszczynski, Bartoszewicz, Hug, Marciniak, and Paczkowski, 2003), thioxanthone (Akat, Gacal, Balta, Arsu, and Yagci, 2010; Tar et al., 2013), quinones, and organic dyes (Aydin et al., 2015). Among them, benzophenones (BPs) have possessed a good reputation as a type II photo-initiator with their hydrogen abstraction ability from after the excitation. The reactive centres generated on the co-initiator compounds initiate the free-radical polymerization to form polymer (Yagci et al., 2010), as depicted in Figure 1. The formed ketyl radical is not able to initiate the radical polymerization due to the relatively stability and steric hindrance of the ketyl radicals and the presence of the effective delocalization of the formed unpaired electron. Additionally, the ketyl radicals might have role in the chain termination during the polymerization by leading to form the polymers bearing the ketyl moieties. The onium salts or certain bromo molecules reacting with ketyl radicals via bromation or oxidation were used as an additives to prevent the chain termination caused by ketyl radicals (Fouassier et al., 1994; Kayaman, Onen, Yagci, and Schnabel, 1994).

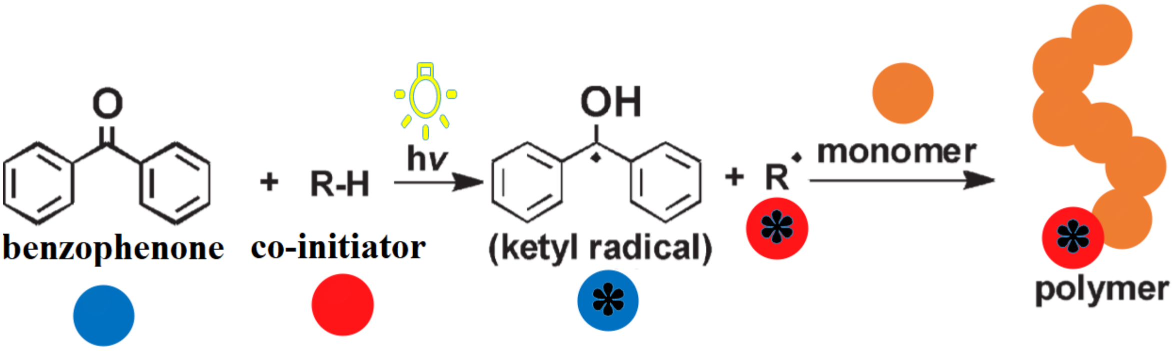

Fig. 1. Simplified representation of Type II photoinitiation mechanism with hydrogen donor and benzophenone

Moreover, the polymerization mechanism allows only the polymerization of the monomers including olefinic double bonds in their molecular structure. Thus, the acrylate and methacrylate monomers were utilized widely in the today polymer industry for the photo-initiated free radical polymerization. It is well-known the fact that they also have different characteristics properties. Namely, polyacrylates have generally rubbery and soft nature by showing lower tensile strength and relatively high elongation, while polymethacrylates are more rigid and stiffer with higher glass temperatures, larger tensile strength and lower elongations since the extra methyl group brings about the formation of sterical hindrance with the restriction of the rotational mobility of the polymer chains in the matrix. Furthermore, the co-initiator (H-donor compounds) used in the type II photo-polymerization explicitly have great importance in terms of the polymerization reaction. That is, the co-initiators reacting rapidly with the photo-initiator excited electronically are selected to produce the reactive radicals initiating the polymerization. It is known that the tertiary amines are more efficiently as a co-initiator when compared to the ethers or alcohols. Thiols are also used commonly as a co-initiators in thiol-ene photo-polymerization systems (Cramer and Bowman, 2001; Hoyle, Lee, and Roper, 2004).

In this present work, we aimed to investigate meticulously the self-initiated photo-polymerization of previously synthesized acrylate and methacrylate monomers (Sainath, Rao, and Reddy, 2000; Soykan and Cetin, 2015), which presenting benzophenone moiety in their molecular structures, by discussing the effects of the three types of the co-initiators (triethylamine, N-methyldiethanolamine and 4,N,N-trimethylanaline) in the different solvents (ethyl acetate, dimethyl sulfoxide and acetone), which were used as reaction medium. It was also aimed to determine the optimal reaction condition to obtain maximum degree of monomer conversion for U1 and U2 monomers

2. Material and Methods (14 pt.)

2.1. Materials

The fundamental chemicals used as a co-initiator in this research, triethylamine (TEA) N-methyldiethanolamine (MDEA) and 4,N,N-trimethylanaline (TMA) were purchased from Alfa Aesar and they were utilized as supplied from company without any further purification. Furthermore, the solvents used in the photo-polymerization reactions, ethyl acetate (EtOAc), dimethyl sulfoxide (DMSO) and acetone were also received from Merck A.G., VWR International and Sigma Aldrich), respectively and they were used without any further purifications. All the other chemicals in this study were analytical grade and used as received without any further purifications.

2.2. Synthesis of the monomers

The syntheses of the monomers, p-benzophenoneoxycarbonylphenyl acrylate (U1) and p-benzophenoneoxycarbonylphenyl methacrylate (U2) were performed in our previously reported studies (Sainath et al., 2000; Soykan and Cetin, 2015). The obtained results regarding to characterization of the monomers with FTIR, 1H-NMR and DSC showed good correlation with the findings founded in these theses conducted in our laboratuvary (Soykan, 2013; Ozturk Sen, 2018).

2.3. UV Polymerization of monomers

The solutions composed of 1.35 mmol of monomer (U1 or U2), 1.35 mmol of co-inititor (TEA, MDEA or TMA) were separately prepared by using the 50 ml of the solvents (DMSO, EtOAc, acetone) for the photo-polymerization. The prepared solutions were added to Pyrex tube that was housed in a water-cooled glass jacket. All reactions were conducted under the deoxygenated and dry nitrogen atmosphere. The samples were irradiated at room temperature for 60 minutes with the use of a high temperature mercury lamp (Hg-Tauchlampe TQ-150, Quarzlampen GmbH, Hanau). At the end of the reactions, the forming polymers in the tube was washed with ethanol (100 ml x 3 times) to remove the residuals rather than the polymer, then filtered and dried in the vacuum at the 50°C for 5-6 hours. The obtained polymers, poly(U1) and poly (U2) were characterized by FTIR, 1H-NMR and DSC and the founded results showed good aggrements with the findings founded in these theses conducted in our laboratuvary (Soykan, 2013; Ozturk Sen, 2018). The degrees of monomer conversions were determined gravimetrically after weighting of the obtained products. All reported data were given as the average value obtained from the least three experiments.

2.4. Instruments

FTIR analyses of the both the monomers and photo polymerization products were conducted by a Shimadzu 8400 S FTIR spectrophotometer in the region ranging from 400 to 4000 cm^{-1}. KBr pellets with roughly 3 mg of sample in 100 mg spectroscopic grade KBr were prepared for FTIR spectra. ^{1}H-NMR spectra of the monomers were recorded from in the deuterated dimethyl sulfoxide (DMSO-d6) by means of Jeol-ECS 400 MHz NMR Spectrometer with Delta software. The chemical shifts values were reported in ppm (part per million) with regarding to the signals of TMS (tetramethylsilane) utilized as an internal reference. The DSC analyses of the U1, U2, poly(U1) and poly (U2) were conducted under nitrogen atmosphere with a heating rate of 10°C/min by using Shimadzu TA-60 WS

Differential Scanning Calorimeter. The data obtained from the instruments related to the characterization of the products depicted the good agreements with the literature (Sainath et al., 2000; Soykan and Cetin, 2015).

3. Results and Discussion

3.1. The effect of co-initiators type on the degree of monomer conversion

In this part of the study, in order to unfold the effect of co-initiator types on the photo-polymerization reaction of the monomers, the photo-polymerization of the U1 and U2 monomers were carried out in EtOAc by using triethylamine (TEA), N-methyldiethanolamine (MDEA) and 4,N,N-trimethylanaline (TMA) co-initiators. The percent conversions of the reactions depending on both monomers and co-initiator types were tabulated in Table 1 and drawn in Figure 2. As for U1 polymers, the obtained results show that the maximum yield was found to be 21.32 % with the use of TEA co-initiator and also the other reaction yields was calculated as 19.89 and 5.64 % for the MDEA and TMA co-initiator, respectively. In addition to that, the yields obtained from the photo-polymerization reactions of the U2 were found to be 17.97, 13.26 and 9.69 % with TEA, MDEA and TMA co-initiators, respectively. It was reported that the aliphatic amine initiators such as triethanolamine had larger initiator efficiency than the aromatic amine initiators such as N-phenyldiethanolamine in the eosin/co-initiator systems in PEGDA monomer (Popielarz and Vogt, 2008). Similarly, it was found that the yields of photo-polymerization reactions conducted with TEA and MDEA as an aliphatic amine initiators were larger than the yields from the reaction with TMA as an aliphatic amine initiators in both monomer types. Furthermore, the results depicted that the sterical effect of the co-initiators played a significant role in the yield of the photo-polymerization reactions. That is, in both U1 and U2 monomers, the maxima were obtained with TEA co-initiator having the relatively smaller steric hindrance, while the minimum yield was obtained with TMA having bulky structure. In other word, the presence of co-initiator having the relatively smaller steric hindrance gave rise to increment in the yield of the photo polymerization reactions of U1 and U2 since the smaller co-initiator initiated the reaction more easily. On the other hand, all reaction yields with U1 monomer was higher than the yields obtained with U2 when compared to the reactions used the same co-initiators. It was attributed that the extra methyl groups in U2 monomer probably played the limiting role in the effective polymerization of the U2 monomer.

Table 1. Comparison of co-initiator efficiency in photoinitiated free radical polymerization

Run	Monomers ($2.7x10^{-2}$ mol L^{-1})	Co-initiator ($2.7x10^{-2}$ mol L^{-1})	Conversion (%)
1	U1	TEA	21.32±0.58
2	U1	MDEA	19.89±0.61
3	U1	TMA	15.64±0.37
4	U2	TEA	17.97±0.11
5	U2	MDEA	13.26±0.39
6	U2	TMA	9.69±0.79

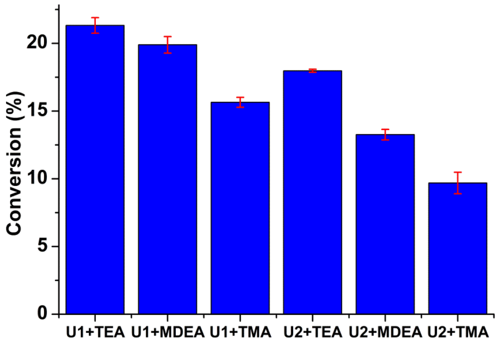

Fig. 2. The dependence of the percent conversion on monomer and co-initiator types.

3.2. The effect of the reaction medium on the degree of monomer conversion

In this section of the study, the dependence of the photo-polymerization reaction yields on the solvents (DMSO, EtOAc, acetone) used in the reactions were investigated. These polar aprotic solvents were preferred for the photo reactions since it was expected that U1 and U2 with polar properties became more reactive and soluble in these polar solvents. The yields obtained from the reactions conducted in the varying solvents with the TEA co-initiator were given in Table 2 and depicted in the Figure 3. It is well-known fact that the characteristics, especially polarity, of the solvents considerable affect both the rate of the free radical polymerization of vinyl monomers and thus the yields of the reactions (Valdebenito and Encinas, 2010). The obtained results showed that the yield of the reactions increased with the increasing of the polarity strength of the solvents (ranked as DMSO>EtOAc>acetone), Figure 3, and the maximum percent conversions, 22.54 % and 19.28 % were found by DMSO solvent for both U1 and U2 monomers, respectively. The minima were also recorded with acetone solvent. These results were attributed to the variation of the interactions between both monomer and solvents and also, radicals and solvents. That is, the solvent having higher polarity (nucleophilic solvent) increased the polarity strength of the monomers, resulted in the decreasing of the electron density of the β-carbon in the acrylate groups presenting in U1 and U2 monomers. Thus, the reactivity of the double bonds increased, which resulted in the higher yields (Czerwinski, 1991a, 1991b). Moreover, the solvents used in the photo-polymerization reactions due to the chain transfer effect had significant role in the activity of formed the radicals. In other words, the presence of the high chain transfer ability of the solvents led to formation of the radicals in the reaction medium, which caused the decrement in the activity of the co-initiator radicals propagating the reactions. Accordingly, the maximum yields were obtained by DMSO having the relatively higher polarity and lower chain transfer due to aprotic character. The other result deduced from the finding was that the yields for U1 was higher than the yields founded from U2 when compared in the same solvents, Figure 3. This probably caused from the molecular structure of U1 and U2 monomer as mentioned above (in section 3.1.). The existence of extra methyl groups in U2 monomer gave rise to the decrement in the yields of the photopolymerization reaction due to the steric hindrance.

Table 2. The yields depending on the solvents used in the photopolymerization reactions

Run	Monomers + Co-initiator (2.7x10^{-2} mol L^{-1})	Solvent (50 ml)	Conversion (%)
7	U1 + TEA	DMSO	22.54±0.36
8	U1 + TEA	EtOAc	21.32±0.18
9	U1 + TEA	Acetone	18.91±0.21
10	U2 + TEA	DMSO	19.28±0.35
11	U2 + TEA	EtOAc	17.97±0.11
12	U2 + TEA	Acetone	15.25±0.65

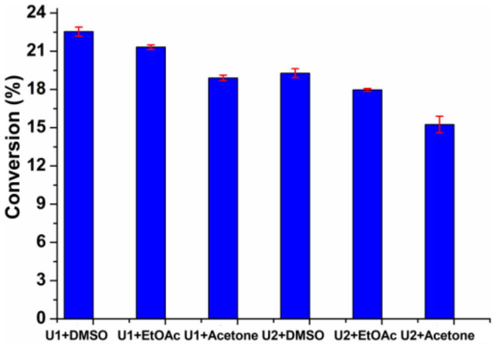

Fig. 3. The dependence of the percent conversion on monomer and co-initiator types.

3.3. The effect of the co-initiator concentration on the degree of monomer conversion

In order to comprehend the optimal co-initiator concentration to achieve the maximum percent conversion, the photo-polymerization reactions for both U1 and U2 were carried out with the use of varying concentration ($2.7x10^{-3}$ M, $13.5x10^{-3}$, $2.7x10^{-2}$ M and $13.5x10^{-2}$ M) of TEA co-initiator by keeping the amount of monomer constant (0.5 g). In photo reactions, DMSO as the solvent and TEA as the co-initiator were used since the maximum yields were recorded at this solvent and co-initiator. The obtained yield findings from the experiments were tabulated in Table 3 and also the variation of degree of monomer conversion with the concentration of co-initiator was depicted in the Figure 4. The results showed that the degree of monomer conversion increased almost linearly with the increasing of the co-initiator concentration from $2.7x10^{-3}$ to $13.5x10^{-2}$ M in the reaction medium for both U1 and U2 monomers. The similar results were founded by Kabatc J. and coworkers (Kabatc, Ortyl, and Kostrzewska, 2017). The maximum values, 31.27 % and 26.10 % were recorded with the $13.5x10^{-2}$ TEA concentration for U1 and U2, respectively. This result was attributed to the increment in the rate of polymerization reaction. Namely, it was known that the rate of photo polymerization increased as the concentration of co-initiator increased in the reaction medium, which resulted in the higher degree of monomer conversion (Schneider, Cavalcante, Consani, and Ferracane, 2009). Similarly, in this current work, the increment in the concentration of co-initiator gave rise to the formation of the relatively higher amount of both triethylamine radicals and ketyl radicals on the U1 and U2 molecules. Thus, collaterally, the increments in the percent conversion of monomers were observed due to presence of larger radicals that initiate the polymerization reaction in the medium. In addition to that, it was deduced from this study that all percent conversion for U1 were distinctively much more than the percent conversions that U2 had when evaluated at the same co-initiator concentration. It was clearly caused from the existence of extra methyl groups in the U2 molecules. The methyl groups created the sterically shielding effect that hinder the radicals from the approaching the carbon-carbon double bond, which ended up the decreasing of the degree of monomer conversion of U2 monomer compared to U1.

Table 3. The relationship between the concentration of the co-initiator and degree of monomer conversion

Run	Monomer Type	Co-initiator (TEA) Concentration	Conversion (%)
13	U1	$2.7x10^{-3}$ mol L^{-1}	15.22±0.15
14	U1	$13.5x10^{-3}$mol L^{-1}	18.46±0.28
15	U1	$2.7x10^{-2}$ mol L^{-1}	22.54±0.36
16	U1	$13.5x10^{-2}$ mol L^{-1}	31.27±0.96
17	U2	$2.7x10^{-3}$ mol L^{-1}	9.68±0.42
18	U2	$13.5x10^{-3}$mol L^{-1}	13.81±0.21
19	U2	$2.7x10^{-2}$ mol L^{-1}	19.28±0.35
20	U2	$13.5x10^{-2}$ mol L^{-1}	26.10±0.55

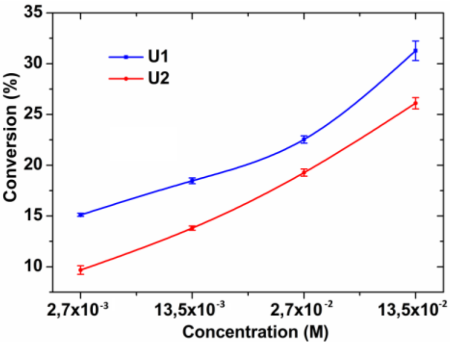

Fig. 4. The dependence of the co-initiator concentration on the degree of monomer conversion

4. Conclusion

In the present work, it was founded that U1 and U2 acrylate monomers bearing the benzophenone pendant unit in their molecular structure had the self-initiator characteristic in the photo-polymerization reaction to form their polymers without any usage of another photo initiator in the reaction medium. Moreover, the dependence of the degree of monomer conversions on the co-initiator type, the solvent and co-initiator concentration were investigated in details. The optimal conditions, at which the maximum percent conversion was recorded, were determined for both U1 and U2. All obtained products (U1, U2, poly(U1) and poly (U2) were characterized via FTIR, 1H-NMR and DSC techniques and the results showed good agreement with the literature. The results also revealed that the optimum photo reaction condition for U1 and U2 was the similar due to the fact that their molecular structure resembled one another, which was 0.5 g of U1 or U2 and $13.5x10^{-2}$ M of TEA co-initiator in 50 ml of DMSO solvent with the 1h of irradiation time at room temperature. Among co-initiator, TEA illustrated the best co-initiator performance due to the fact that it was aliphatic amine and had relatively the lowest steric hindrance when compared to other co-initiators Furthermore, the findings also showed that the degree of monomer conversion for U1 and U2 increased as the polarity strength of the solvents (DMSO>EtOAc>acetone). It was attributed to that the carbon-carbon double bond in the polar monomer became more reactive when dissolved in more polar solvents. Additionally, the percent conversion increased almost linearly with the increasing of the co-initiator concentration in the reaction medium. This was presumably stemmed from the formation of the relatively higher amount radicals during the photo-reaction, which resulted in the increasing of the photo-polymerization reaction rate and the degree of monomer conversion.

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