Synthesis and Characterization of Free and Grafted N-Halamine Nanoparticles for Decomposition of Organic Dyes in an Aqueous Continuous Phase

Chen Gelber and Shlomo Margel*

ABSTRACT: Synthetic organic dyes constitute a major pollutant in wastewater. Here, we describe the synthesis and characterization of N-halamine nanoparticles (NPs) for decomposition of organic dyes from contaminated wastewater. Cross-linked poly-(methacrylamide) (PMAA) NPs of hydrodynamic diameters ranging from 11 ± 1 to 161 ± 31 nm were synthesized at room temperature by redox surfactant-free dispersion copolymerization of methacrylamide and the cross-linking monomer N,N′-methylenebis-(acrylamide) in an aqueous continuous phase. The effect of various polymerization parameters on the diameter and size distribution of the formed NPs was studied. Additionally, thin coatings composed of cross-linked PMAA NPs were grafted onto oxidized corona-treated polypropylene (PP) films by redox graft polymerization of the monomers in the presence of oxidized PP films. The free and grafted NPs were converted to N-halamine species by chlorination with sodium hypochlorite. The decomposition kinetics of two model organic dyes, methylene blue (MB) and crystal violet (CV), was evaluated for both free and grafted PMAA−Cl NPs. Free cross-linked PMAA−Cl NPs at room temperature, with concentrations of 5 and 0.5 mg/mL, illustrated full decomposition of CV and approximately 90% decomposition of MB after 42 and 97 h. In order to enhance the dye decomposition, the mixtures were heated to 70 °C. Complete decomposition of CV and MB at PMAA−Cl NP concentrations of 5 and 0.5 mg/mL required 60 and 240 min for CV, respectively, and 180 and 420 min for MB, respectively. Similarly, the PP/PMAA−Cl films also demonstrated a high reduction in the MB concentration after 150 min. Due to the highly efficient dye decomposition, these free and immobilized chlorinated NPs may be utilized as new reagents for decomposition of organic materials from contaminated wastewater.

1. INTRODUCTION

Synthetic organic dyes are widely used in industries such as paper, textile, leather, cosmetics, additives, food, and analytical chemistry.1,2 The environmental impact of these industries is due to the large production of wastewater that contain organic dyes and other contaminants.3 These compounds pose a threat to aquatic life, and their presence in drinking water has a potentially harmful effect on public health. Furthermore, organic dyes cause coloration of water.1,4,5 Therefore, it is essential to remove dyes from water or to treat them in order to minimize their effect on the environment.4 Conventional biological treatments are ineffective due to the high stability of the dyes, which typically contain several aromatic rings.6 Different approaches were investigated for removal of dyes from water such as physical adsorption, coagulation, biological decoloration, oxidation processes, photo-Fenton reaction, ion exchange, membrane filtration, and ozone treatment.1,4,7 Activated carbon is used as an adsorbent for the removal of contaminations from wastewater. Activated carbon has a disadvantage due to its high cost of activity regeneration.8 In recent years, intensive research has been done on chitosan in order to commercialize it as an alternative adsorbent to activated carbon. Chitosan, in different forms, was investigated for a low-cost, environmentally friendly, simple, and effective adsorbent dye removal.9 One of the most effective methods is termed advanced oxidation processes (AOPs), whereby hydroxyl radicals are generated in a sufficient amount for water treatment. The radicals break the chromophoric dye molecules into smaller nonchromophoric ones, resulting in decomposition of the dye.3,5,7,10−12 The previously published methods are not cost effective for large-scale production; therefore, there is a need to develop efficient and environmentally friendly methods that incur considerably lower costs.2,13

N-Halamine compounds contain one or more nitrogen−halogen covalent bonds; they were extensively researched in...
the last decades due to their antibacterial activity.14−16 N-Halamines are relatively cheap, weakly toxic to humans and the environment, can be regenerated, and exhibit long-term stability in aqueous solutions.16−21 The selective antibacterial activity of N-halamines involves generation of hydroxyl radicals, reactive oxygen species (ROS), upon exposure to organic media. Such ROS are not generated upon exposure to water, indicating a specific mode of action.19 To the best of our knowledge, there is no report on degradation of organic materials by N-halamine species.

In this study, we used the advantages of N-halamines as a new generator of AOP to deal with the problem of water contamination by organic materials. The manuscript describes the synthesis at room temperature of cross-linked poly-(methacrylamide) (PMAA) NPs by redox surfactant-free copolymerization of methacrylamide (MAA), a monomer with a primary amide group with N,N′-methylenebis(acrylamide) (MBAA), a cross-linking monomer with a secondary amide, in an aqueous continuous phase using sodium bisulfite as redox initiator. This synthesis at room temperature presents an improvement compared to the previously reported procedure.21 The effect of various polymerization parameters on the diameter and size distribution of the formed NPs was also studied. Polypropylene (PP) films were subjected to a thin coating of cross-linked PMAA NPs (PP/PMAA) using a simple and efficient method of redox
The graft polymerization of the monomers MAA and MBAA onto the corona-treated film surface. The effect of two different monomer weight ratios on the formed grafted films was illustrated. N-Halamine derivatives of cross-linked PMAA NPs and PP/PMAA films were produced using household bleach. The activity of the chlorinated free and grafted PMAA–CI NPs in decomposition of organic materials was evaluated using two model organic dyes, methylene blue (MB) and crystal violet (CV).

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Cross-Linked PMAA NPs. Cross-linked PMAA NPs were prepared by redox surfactant-free copolymerization of MAA and MBAA at room temperature, as described in the Experimental Section (Figure 1). The polymerization yield of cross-linked NPs was found to be 82%, and after addition of SBS, the yield was increased to 100%, as confirmed by HPLC analysis. The dry and hydrodynamic size of the NPs was evaluated using high-resolution scanning electron microscopy (HR-SEM) and dynamic light scattering (DLS), respectively. The dry diameter of NPs synthesized with 50% of the cross-linking monomer MBAA was 16 ± 5 nm (Figure 2A), and their hydrodynamic diameter was 39 ± 5 nm (Figure 2B). Larger cross-linked NPs with a dry diameter of 46 ± 12 nm (Figure 2C) and a hydrodynamic diameter of 135 ± 23 nm (Figure 2D) were also synthesized with a higher MBAA ratio of 70%. The significantly smaller dry diameter is probably due to the hydrophilic nature of the PMAA NPs. The hydrodynamic diameter takes into account the water molecules adsorbed on the surface and within the NPs, as well as the Brownian motion.22,23

2.2. Chlorination of Cross-Linked PMAA NPs. Conversion of the cross-linked PMAA NPs to N-halamine-chlorinated derivatives denoted by PMAA–CI was performed using sodium hypochlorite, as described in Figure 1 (either one or both hydrogen of NH\textsubscript{2} can be substituted by Cl atoms). The chlorine concentrations in the 5 mg/mL PMAA–CI NP solutions prepared with 50 and 70% of the cross-linker monomer MBAA were found to be 19 and 25 mM, respectively. Figure 3 includes the expected N\textsubscript{H}N\textsubscript{H}C\textsubscript{Cl} stretching band, the N\textsubscript{H}N\textsubscript{H}C\textsubscript{Cl} symmetric and asymmetric stretching, respectively. Figure 3A shows the FTIR spectra of (A) cross-linked PMAA and (B) PMAA–CI NPs; in both cases, the peaks are well-known in the literature.16,21 Figure 3A presents the FTIR spectrum of the PMAA–CI NPs, which differs slightly from the spectrum of the nonchlorinated NPs. The peaks at 3473 and 3448 cm\textsuperscript{-1} are nearly disappeared and replaced by a new sharp peak at 880 cm\textsuperscript{-1}, corresponding to the N–H stretching band, the N–H band, and the carbonyl stretching band, respectively, and the peaks at 1648 and 3473 cm\textsuperscript{-1} of NH\textsubscript{2} symmetric and asymmetric stretching, respectively. Figure 3B presents the FTIR spectrum of the PMAA–CI NPs, which is nearly disappeared and replaced by a new sharp peak at 880 cm\textsuperscript{-1}, corresponding to the N–Cl stretching band. The peaks in Figure 3A at 1212, 1532, and 1655 cm\textsuperscript{-1}, corresponding to C–N, N–H, and C=O vibrations, shifted slightly to 1207, 1536, and 1668 cm\textsuperscript{-1}, respectively. These findings could probably be explained by the replacement of N–H by N–Cl.16,21

The chlorination of the cross-linked PMAA NPs was also confirmed using elemental analysis, as summarized in Table 1. The measurements show that the chlorination process mainly changed the C, N, and Cl contents after chlorination of NPs synthesized with 50 or 70% MBAA. The N content decreased by 5.7 or 4.7%, and the C content decreased by 6.2 or 4.2%. The Cl content in both cases was increased significantly, about 11.5% (previously 0.0%), indicating that the chlorination was successful.

2.3. Polymerization Kinetics. The kinetics of the polymerization with 50 and 70% of the cross-linking monomer MBAA was evaluated by following the hydrodynamic diameter and size distribution of the produced NPs over time, as shown in Figure 4. During the first 30 min, NPs were not detected in the reaction mixture; up to 120 min, there was a sharp increase in the average size of the produced NPs followed by a much milder increase over the next few hours. For example, the hydrodynamic diameters of NPs prepared with 50% MBAA increased from 14 ± 2 to 19 ± 2 and 35 ± 4 nm after 60, 120,
and 360 min, respectively. The NPs prepared with 70% MBAA showed significantly faster growth, and after 60, 120, and 360 min of polymerization, the hydrodynamic diameter increased from 60 ± 8 to 115 ± 17 and 131 ± 21 nm, respectively. The particles reached their final diameter after about 24 h.

2.4. Effect of Polymerization Parameters on NP Diameter, Size Distribution, and Yield. 2.4.1. [NaHSO₃]/[APS] Mole Ratio. The effect of the [NaHSO₃]/[APS] mole ratio was studied for cross-linked PMAA NPs with a 1:1 mole ratio between the two monomers (Figure 5). Figure 5A illustrates the hydrodynamic diameter and size distribution of NPs formed with different mole ratios; up to a ratio of 3, no detected NPs were formed in the solution. Progressively higher ratios resulted in smaller NPs with decreased size distribution; for example, increasing the mole ratio from 5 to 10 to 15 resulted in significantly smaller diameters of 89 ± 12 to 48 ± 6 and 32 ± 3 nm, respectively. Figure 5B presents the yield of the formed cross-linked PMAA NPs with different mole ratios, showing an optimal yield of 75% at a ratio of 10, significantly higher than the yields at ratios of 5 (57%) and 15 (63%). The present study was then continued with this optimal mole ratio.

2.4.2. Effect of Total Monomer Concentration. The effect of the total monomers concentration, MAA and MBAA, on the diameter and size distribution of the formed cross-linked NPs, while maintaining a 1:1 weight ratio between the two monomers and the other polymerization parameters constant, was investigated with 50% MBAA (Figure 6A). Contrary to previous publications, the system was relatively stable, and preparation of NPs was possible at concentrations above 3%. Figure 6A illustrates that higher concentrations result in increased diameters: when increasing the total monomer concentration from 2 to 3% (w/v), the diameter and size distribution of the NPs increases significantly from 39 ± 5 to 110 ± 16; further increase to 4% results in a slightly larger diameter and size distribution of 139 ± 25 nm. Experiments with monomer concentrations above 4.4% could not be performed due to insolubility of the MBAA monomer in the continuous phase. As previously reported for dispersion polymerization, higher monomer concentrations also lead to an increase in both reaction rate and polymer yield. One explanation is that the initial solubility of the reaction medium increases such that the formed oligomers grow into longer chains before precipitating, thereby resulting in larger particles.

2.4.3. Effect of MBAA Weight Ratio [MBAA]/([MAA] + [MBAA]). The effect of the MBAA weight ratio, [MBAA]/([MAA] + [MBAA]), on the diameter and size distribution of the formed cross-linked PMAA NPs at a constant total monomer concentration (2%) is shown in Figure 6B. No NPs were detected at a weight ratio below 20%. The greater weight ratio resulted in larger NPs with greater size distribution. For example, when increasing the weight ratio from 20 to 40 to 60% (w/w), the diameter and size distribution increases from 11 ± 1 to 22 ± 3 to 99 ± 14 nm, respectively. This increase in diameter and size distribution could be explained by the higher hydrophilicity of MBAA with respect to MAA, which leads to a greater amount of absorbed water molecules on the NPs surface, resulting in a larger hydrodynamic diameter. In the experiment, no agglomeration was observed in contrast to previous publications, which indicates the stability of the polymerization system.

2.4.4. Effect of the Initiator Type and Concentration. The effect of the initiator type, APS or PPS, and concentration on the diameter and size distribution of the formed cross-linked PMAA NPs was also studied, as shown in Figure 6C. When

Figure 5. Effect of [NaHSO₃]/[APS] mole ratio on (A) the hydrodynamic size and (B) polymerization yield of cross-linked PMAA NPs.

Figure 6. Effect of (A) total monomer concentration, (B) MBAA weight ratio, and (C) initiator type and concentration on the diameter and size distribution of the formed cross-linked PMAA NPs.
increasing the initiator concentration, the diameter and size distribution of the NPs decreased. For example, while increasing the APS concentration from 2 to 5 to 10% (w/w), the NPs diameter and size distribution decreased from 42 ± 4 to 28 ± 3 to 16 ± 2 nm. The same behavior was observed when the PPS concentration increased from 2 to 5 to 10% (w/w). The NP diameter and size distribution decreased from 46 ± 6 to 31 ± 4 to 18 ± 2 nm. These results are surprising, as they differ from those previously reported for polymeric NPs composed of MAA and MBAA monomers; they could be explained by an increase in oligoradical concentration due to the higher initiator concentration. Therefore, a greater number of smaller chains are produced and precipitate as particles, resulting in a decrease in the particle diameter.26–28

2.5. Graft Copolymerization of MAA and MBAA Monomers onto Oxidized PP Films. 2.5.1. Synthesis of PP/PMAA and PP/PMAA−Cl Films. PP/PMAA films were prepared at room temperature by graft dispersion copolymerization of MAA and MBAA in an aqueous phase in the presence of an oxidized PP film, as described in the Experimental Section. The conversion of the PP/PMAA films to the N-halamine chlorinated species, PP/PMAA−Cl, was performed using sodium hypochlorite, as described in the Experimental Section. The chlorine concentration on the PP/PMAA−Cl films synthesized with 50 and 70% of the cross-linking monomer MBAA, respectively. Figure 7 shows typical attenuated total reflectance infrared (ATR-IR) spectra of PP, PP/PMAA, and PP/PMAA−Cl films, formed with 50% MBAA. All spectra demonstrated typical peaks of the PP film: 2953 and 1456 cm⁻¹ corresponding to CH₂ asymmetrical stretching, 2872 and 1374 cm⁻¹ corresponding to CH₃ symmetrical stretching, and 2916 and 2839 cm⁻¹ corresponding to CH₃ asymmetrical and symmetrical stretching bands.29,30 The thin films grafted with cross-linked PMAA NPs (Figure 7B) demonstrated new peaks, at 1213 cm⁻¹ corresponding to C–N stretching, 1536 and 1662 cm⁻¹ corresponding to the N–H band and carbonyl stretching, and a broad peak at 3358 cm⁻¹ corresponding to NH₂ symmetric and asymmetric stretching, respectively. The ATR-IR spectrum of the PP/PMAA−Cl film (Figure 7C) is similar to the spectrum of the PP/PMAA film, with two exceptions: the broad peak at 3358 cm⁻¹ nearly disappears, and the peaks at 1213 and 1536 cm⁻¹, corresponding to C–N and N–H vibrations, shifted slightly to 1206 and 1533 cm⁻¹, respectively. These findings could probably be explained by the replacement of the N–H bond by N–Cl.16,21,31 The ATR-IR spectra of the films formed with 70% MBAA exhibit the same peaks shown in Figure 7.

2.5.2. Characterization of PP/PMAA and PP/PMAA−Cl Films. Figure 8 demonstrates the topography of the different films, obtained by AFM measurements—PP, oxidized PP, PP/PMAA and PP/PMAA−Cl (prepared with 50 and 70% MBAA). Figure 8A reveals that the surface of the PP films is quite rough, with an average Rq value of 5.7 ± 0.4 nm. Oxidized PP films (Figure 8B) treated by air corona showed a slightly higher roughness of 6.1 ± 0.5 nm, attributed to collisions of oxygen ions with the film that creates pores in the PP film. After graft polymerization, cross-linked PMAA NPs were obtained on the surface of the oxidized films. The diameter and size distribution of the NPs were found to be 28.5 ± 2.4 and 42.1 ± 1.7 nm for 50 and 70% MBAA, respectively (Figure 8C,E), with a lower roughness of 4.3 ± 0.5 and 5.1 ± 0.9 nm, respectively, explained by the shape of the grafted NPs, which fill the pores on the oxidized film surface. After chlorination, cross-linked NPs are still observed on the films, and the surface roughness is similar to the non-chlorinated films (Figure 8D,F).

The surface elemental analysis of the films obtained by XPS measurements is presented in Table 2. The XPS survey spectrum of the PP and oxidized PP films shows intense carbon (C₁s) and oxygen (O₁s) peaks at 285 and 531 eV, respectively, along with a small peak at 400 eV corresponding to nitrogen (N₁s). The spectrum of the thin films grafted with cross-linked PMAA NPs shows intense carbon (C₁s), nitrogen (N₁s), and oxygen (O₁s) peaks at 285, 400 and 531 eV, respectively. The spectrum of the PP/PMAA−Cl films demonstrated the same peaks and an additional peak at around 200 eV, corresponding to Cl₂p.32 The increased amount of N₁s and O₁s in the PP/PMAA spectrum demonstrates the successful grafting of the PMAA NPs on the PP film surface. The new peak corresponding to Cl₂p, which only appeared in the spectrum of the PP/PMAA−Cl films, indicates the successful chlorination of the PP/PMAA films to form N-halamine species. The wettabilities properties of the different films were measured by a water contact angle using the sessile drop method. Table 3 exhibits the static contact angles on PP, oxidized PP, and thin films grafted with cross-linked PMAA and PMAA−Cl NPs. After air corona treatment, the contact angle of the PP films decreased from 80.0 ± 1.2 to 70.3 ± 4.3° due to formation of polar groups on the surface of the films. After graft polymerization, the PP/PMAA films showed a
decrease in contact angle to 52.5 ± 4.4 and 10.7 ± 2.8°, for films prepared with 50 and 70% MBAA, respectively. The decrease in contact angle after graft polymerization is probably due to the hydrophilic nature of the cross-linked PMAA NPs grafted on the surface of the films. The lower contact angles at the higher MBAA concentration can be attributed to the larger diameter of the grafted NPs and the high roughness of the film. After chlorination, the PP/PMAA−Cl films showed an increase in the contact angle to 72.7 ± 4.2 and 64.8 ± 4.0° for films prepared with 50 and 70% MBAA, respectively. The increase in the contact angle after chlorination is probably due to the hydrophobicity of the N−Cl bond compared to the N−H bond.

2.6. Enhanced Decomposition of Organic Dyes by Cross-Linked PMAA−Cl NPs and PP/ PMAA−Cl Films. 2.6.1. Enhanced Decomposition of Organic Dyes by Cross-Linked PMAA−Cl NPs. The decomposition experiments investigated the degradation kinetics of two model dyes, MB and CV in aqueous solutions, by the free cross-linked PMAA−Cl NPs prepared with 50 and 70% of the cross-linking monomer MBAA. The decomposition rates of MB and CV were evaluated by following the absorption over time with a UV−visible spectrophotometer at 664 and 590 nm, respectively. Figure 9 shows the decomposition rate by the cross-linked PMAA−Cl NPs with a concentration of 5 mg/mL (Figure 9A) and 0.5 mg/mL (Figure 9B) at room temperature. The figure shows that during the first 7 h of the experiment, there is a sharp decrease in the rate of decomposition followed by a much milder decrease over the following hours. After 42 and 97 h, at a concentration of 5 and 0.5 mg/mL, respectively, CV decomposed entirely, while 5−8 and 9−13% of MB did not decompose, and dyes treated with DDW and non-chlorinated NPs showed no detected decomposition.

In order to speed up the dye decomposition, the mixtures with cross-linked PMAA−Cl NPs were heated to 70 °C. Figure 10 demonstrates the decomposition rate at concentrations of 5 (Figure 10A) and 0.5 mg/mL (Figure 10B), showing the same behavior observed at room temperature, a sharp decrease in the decomposition rate followed by a much milder decrease. Complete decomposition of CV required 60 and 240 min with NPs at concentrations of 5 and 0.5 mg/mL, respectively, while MB required much longer durations of 180 and 420 min. Cross-linked PMAA−Cl NPs prepared with 70% MBAA showed lower reduction in the decomposition rate compared to NPs prepared with 50% MBAA. This may be attributed to the smaller size of the NPs prepared with 50% of the cross-linking monomer, which results in a higher surface area and enhanced activity.25,33 The reduction in the dye concentration is mainly due to their decomposition by hydroxyl radicals formed upon exposure to organic media.19 Different

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Table 2. Elemental Concentration of PP, Oxidized PP, PP/PMAA, and PP/PMAA−Cl Films Obtained from XPS Measurements

| film type | % MBAA | elemental concentration (%) | C1s | N1s | O1s | Cl2p |
|-----------|--------|-----------------------------|-----|-----|-----|------|
| PP        | 86.3   | 1.9                         | 10.6| 0.0 |     |      |
| oxidized PP | 85.7   | 2.1                         | 10.6| 0.4 |     |      |
| PP/PMAA   | 76.3   | 2.6                         | 20.0| 0.2 |     |      |
| PP/PMAA−Cl| 74.7   | 4.4                         | 17.4| 2.8 |     |      |
| PP/PMAA   | 81.8   | 6.3                         | 11.8| 0.2 |     |      |
| PP/PMAA−Cl| 80.5   | 7.0                         | 11.4| 3.0 |     |      |

Table 3. Static Contact Angles of Water onto PP, Oxidized PP, PP/PMAA, and PP/PMAA−Cl Films

| film type | % MBAA | static contact angle (°) |
|-----------|--------|--------------------------|
| PP        | 80.0 ± 1.2 |                           |
| oxidized PP | 70.3 ± 4.5 |                           |
| PP/PMAA   | 52.5 ± 4.4 |                           |
| PP/PMAA−Cl| 72.7 ± 4.2 |                           |
| PP/PMAA   | 64.8 ± 2.8 |                           |
| PP/PMAA−Cl| 64.8 ± 4.0 |                           |

Figure 8. AFM images of (A) PP, (B) oxidized PP, (C, D) PP/PMAA, PP/PMAA−Cl (50% MBAA) and (E, F) PP/PMAA, PP/PMAA−Cl (70% MBAA) films.

Figure 9. AFM images of (A) PP, (B) oxidized PP, (C, D) PP/PMAA, PP/PMAA−Cl (50% MBAA) and (E, F) PP/PMAA, PP/PMAA−Cl (70% MBAA) films.

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| PP/PMAA   | 64.8 ± 2.8 |                           |
| PP/PMAA−Cl| 64.8 ± 4.0 |                           |
mechanisms of dye degradation by hydroxyl radicals were previously reported in the literature.34−37

2.6.2. Enhanced Decomposition of Organic Dyes by PP/PMAA−Cl Films. The activity of thin films grafted with cross-linked PMAA−Cl NPs for decomposition of organic materials was also evaluated using MB as a model dye. The different films (3.5 × 8 cm²) were shaken with an MB solution, as described in the Experimental Section. MB decomposition was measured after 2.5 h, and the results are shown in Table 4. MB with PP/PMAA films served as the control. As shown in the table, nonchlorinated films show relatively small reduction in MB concentration (about 15%), probably resulting from adsorption of MB on the surface of the PP/PMAA film. On the other hand, PP/PMAA−Cl films show 83% and 76% reduction in MB concentration for films prepared with 50 and 70% MBAA, respectively. The reduction in MB concentration is mainly due to decomposition of the dye by ROS.19 The PP/PMAA−Cl films prepared with 50% MBAA have smaller NPs on the surface of the film, resulting in enhanced activity.

Table 4. MB Concentrations after 2.5 h at Room Temperature with PP/PMAA and PP/PMAA−Cl Films

| film type | % MBAA | MB concentration (molar %) |
|-----------|--------|-----------------------------|
| PP/PMAA   | 50     | 84                          |
| PP/PMAA−Cl| 50     | 17                          |
| PP/PMAA   | 70     | 88                          |
| PP/PMAA−Cl| 70     | 24                          |

3. SUMMARY AND CONCLUSIONS

Cross-linked PMAA NPs were synthesized by redox surfactant-free copolymerization of MAA and MBAA in an aqueous continuous phase. The effect of different polymerization parameters on the diameter and size distribution of the produced cross-linked PMAA NPs was studied. Thin coatings of these NPs were prepared by redox graft polymerization of the MAA and MBAA monomers onto corona-treated PP films. The free and grafted NPs were chlorinated to N-halamine species using sodium hypochlorite. Decomposition experiments investigated the degradation kinetics of two model dyes, MB and CV in aqueous solutions, by the cross-linked PMAA−Cl NPs at both room temperature and 70 °C. Three conclusions can be derived from the results: first, CV is more sensitive and decomposes faster than MB in the presence of these NPs. Second, the dyes decomposition at 70 °C is faster compared to room temperature. Third, chlorinated NPs prepared with 70% MBAA showed less decomposition compared to those prepared with 50% MBAA, in accordance with the smaller size and higher surface area of the latter NPs. Thin films grafted with PMAA−Cl NPs showed 83% and 76% reduction in MB concentration. The results show promising activity of the free and grafted chlorinated NPs in decomposition of organic model dyes. These NPs and grafted...
films can therefore be considered and utilized as useful new reagents for decomposition of organic materials from contaminated wastewater.

The excellent activity of the free and grafted N-haline NPs in the dye decomposition experiments is due to the hydroxyl radicals, which are formed when the cross-linked PMAA–Cl NPs are exposed to organic materials. Different mechanisms of dye degradation by hydroxyl radicals were previously reported in the literature.21–31 For potential application in wastewater, it is important to know the toxicity of the decomposition products, which may be more dangerous than the pollutant itself. This field of research requires more experimental evidence, since the mechanisms and exact structures of many reported compounds have not been investigated. In a future work, we plan to extend the present study in order to improve our understanding of the mechanism, intermediates, and products generated during the dye decomposition demonstrated in the present manuscript.

4. EXPERIMENTAL SECTION

4.1. Materials. The following analytical grade chemicals were used without further purification: methacrylamide (MAA), N,N'-methylenebis(acrylamide) (MBAA), potassium persulfate (PPS), ammonium persulfate (APS), sodium bisulfite (NaHSO3) solution (SBS), sodium hypochlorite solution (NaOCl, 5%), acetic acid (AcOH), sodium iodide (NaI), sodium thiosulfate (0.1 N), methylene blue (MB) solution (1.5%), and crystal violet (CV) solution (1%), which were purchased from Sigma-Aldrich (Rehovot, Israel); and PP films (air corona treated) of A4 size and 50 μm thickness, which were obtained from Hanita Coatings RCA Ltd. (Hanita, Israel). Deionized water was purified by passing through an Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK).

4.2. Synthesis at Room Temperature of Cross-Linked PMAA NPs by Redox Dispersion Copolymerization. Cross-linked PMAA NPs with hydrodynamic diameter ranging from 11 ± 1 to 161 ± 31 nm were prepared by redox surfactant-free dispersion copolymerization of the monomers MAA and MBAA. Figure 1 illustrates the chemical structures of the monomers and formed cross-linked PMAA NPs. The obtained NPs contained both primary amides (of MAA) and secondary amides (of MBAA); the resulting two types of haloamides in the NP structure were expected to increase the secondary amides (of MBAA); the resulting two types of amides (of MAA) and formed cross-linked PMAA NPs. The polymerization yield was calculated by taking the ratio of the weights of the two monomers.

4.3. Graft Polymerization of MAA and MBAA onto Oxidized PP Films. A two-step process was used in order to prepare a thin coating of cross-linked PMAA NPs on the surface of a PP film. In the first step, in order to improve adhesion of the coating to the PP surface, the film was oxidized by corona treatment with iCorona-I (Vetaphone Corona & Plasma, Denmark) at 300 W·min−2. In the next step, redox graft polymerization of the NPs onto the oxidized film was conducted as follows: the film was placed in a 20 mL aqueous solution containing 2% (w/v) of the monomers MAA and MBAA and 3% (w/w) of the initiator APS. Two monomer weight ratios were used. Polymerization was initiated by adding SBS with a mole ratio of 10 with respect to APS. The mixture was then stirred at room temperature for 24 h. The formed PP/PMAA films were washed of excess reagents with distilled water and then dried with nitrogen gas.

4.4. Chlorination of Cross-Linked PMAA NPs and Graft Polymerized PP/PMAA Films. 4.4.1. Chlorination of Cross-Linked PMAA NPs. The chlorinated PMAA NPs were prepared using sodium hypochlorite, as previously reported in the literature.21 In brief, a sodium hypochlorite aqueous solution (5 mL, 5% w/v) was added to an aqueous dispersion of cross-linked PMAA NPs (5 mL, 15 mg/mL), and the dispersion was shaken at room temperature for 1 h. Excess sodium hypochlorite was removed from the obtained PMAA–Cl NPs dispersion by extensive dialysis against water. The bound chlorine content of the cross-linked PMAA–Cl NPs was determined by iodometric/thiosulfate titration according to the literature21 as follows:

\[
[\text{Cl}^-](\text{mM}) = \frac{N \times V \times 1000}{2}
\]

where N is the normality (equiv/L) and V is the volume (L) of the titrated sodium thiosulfate solution.

4.4.2. Chlorination of Thin Films Grafted with Cross-Linked PMAA NPs. Sodium hypochlorite aqueous solution (25 mL, 2% w/v) was added to a 50 mL centrifuge tube containing the PP/PMAA films and shaken at room temperature for 1 h. The formed PP/PMAA–Cl films were washed of excess reagents with distilled water and then dried with nitrogen gas. The bound chlorine content on the PP/PMAA–Cl films was determined by adding a coupon of the film (2 × 2 cm2) to a sodium iodide solution and measuring the colored solution by a spectrophotometer at 292 and 350 nm.30,40

4.5. Characterization of Cross-Linked NPs and PP Films. Dried particle diameters and size distributions were measured with high-resolution scanning electron microscopy (HR-SEM, 400 L, FEI, Magellan). For this purpose, a drop of dilute NP dispersion in distilled water was spread on a glass surface and dried at room temperature. The average particle size and size distribution were determined by the measurement of the diameter of more than 200 particles by image analysis software (Image J). Hydrodynamic diameters and size distributions of NPs dispersed in double distilled water (DDW) were measured by a Nanophox particle analyzer (SympatecGmbH, Germany).

Fourier transform infrared (FTIR) analysis was performed using a Bruker Platinum FTIR Quick-Snap TM sampling module A220/D-01 with 13 mm KBr pellets composed of 2 mg of the detected material (cross-linked PMAA NPs) and 198 mg KBr. The analysis of the grafted thin films was performed by the attenuated total reflectance (ATR) technique. All samples were scanned over 48 times at 4 cm−1 resolution.

Elemental analysis was performed using a Thermo FLASH 2000 organic elemental analyzer by the analytical laboratories of the Hebrew University, Jerusalem. Halogen content was determined using the oxygen-flask combustion method,
Surface topography analysis of the unmodified and grafted thin films was done by atomic force microscopy (AFM). AFM measurements were carried out using a Bio FastScan scanning probe microscope (Bruker AXS, Santa Barbara, CA). All images were obtained using peak force mode with a Fast Scan C (Bruker) silicon probe with spring constant of 0.8 N/m. The resonance frequency of the cantilever was approximately 300 kHz (in air). Measurements were performed in ambient conditions. Scans for each film were performed on an area of 3 × 3 μm using the ScanAsyst mode with a 1.6 Hz scan rate. The resolution of the images was 512 samples per line. Image processing and roughness analysis were performed using NanoScope Analysis software. Before roughness analysis, the “flattening” and “planarizing” functions were applied to each image. The morphological changes of the films were determined by the root mean square roughness (Rq) values averaged over three different regions on each film. Diameters and size distributions of the grafted PMAA NPs on the PP films were determined using AFM images based on over 200 NPs.

X-ray photoelectron spectroscopy (XPS) measurements for surface elemental analysis of the films were conducted using a Thermo Fisher Nexsa surface analysis system with a monochromated Al Kα X-ray source.

Sessile drop water contact angle measurements were done using a goniometer (System OCA, model OCA20, Data Physics Instruments GmbH, Filderstadt, Germany). Drops of 5 μL of distilled water were placed on five different areas of each film, and images were captured a few seconds after deposition. The static water contact angle values were determined by Laplace–Young curve fitting. All measurements were performed at 25 °C and 60% humidity. Unmodified and oxidized PP films were used as reference.

Decomposition of the organic dyes MB and CV was tracked by recording the absorption spectra with a Cary 100 UV–Vis spectrophotometer (Agilent Technologies Inc.).

4.6. Enhanced Decomposition of Organic Dyes by Free and Grafted Cross-Linked NPs. 4.6.1. Enhanced Decomposition of Organic Dyes by Cross-Linked PMAA−Cl NPs. The activity of the cross-linked PMAA−Cl NPs for decomposition of organic materials was evaluated using two organic dyes as a model, methylene blue (MB) and crystal violet (CV). MB and CV solutions with a final concentration of 0.1 mg/mL were prepared by dilution with DDW. A total of 1.8 mL of chlorinated NPs at two different concentrations, 5 and 0.5 mg/mL, were added to 0.2 mL of MB or CV solutions, and the mixtures were shaken at 25° and 70 °C until all of the dye decomposed. The decomposition was evaluated by following the absorption with a UV–Vis spectrophotometer at 664 and 590 nm, respectively. Dyes treated with DDW and nonchlorinated NPs served as negative controls.

4.6.2. Enhanced Decomposition of Organic Dyes by PP/PMAA−Cl Films. The activity of the PP/PMAA−Cl grafted films in decomposition of organic materials was also evaluated using the organic dye MB. A solution of MB with a final concentration of 0.001 mg/mL was prepared by dilution of the MB solution with distilled water. The films (3.5 × 8 cm<sup>2</sup>) were placed in a petri dish with 7 mL of the dye solution, and the plates were gently shaken at 25 °C for 2.5 h. Decomposition of MB was evaluated by following the absorption peak at 664 nm. MB treated with PP/PMAA film served as control.

**REFERENCES**

(1) Alshamsi, F. A.; Albadwawi, A. S.; Alnuaimi, M. M.; Rauf, M. A.; Ashraf, S. S. Comparative Efficiencies of the Degradation of Crystal Violet Using UV/Hydrogen Peroxide and Fenton’s Reagent. Dyes Pigm. 2007, 74, 283–287.

(2) Pardo, A.; Garcia, H.; Ramirez, P.; Carrillo-Alvarado, M. A.; Krishna, K. S.; Dominguez, N.; Islam, M. T.; Wang, H.; Noveron, J. C. Self-Regenerating Photocatalytic Hydrogel for the Adsorption and Decomposition of Methylene Blue and Antibiotics in Water. Environ. Technol. Innovation 2018, 11, 321–327.

(3) Batista, A. P. L.; Carvalho, H. W. P.; Luz, G. H. P.; Martins, P. F. Q.; Gonçalves, M.; Oliveira, L. C. A. Preparation of CuO/SiO<sub>2</sub> and Photocatalytic Activity by Degradation of Methylene Blue. Environ. Chem. Lett. 2010, 8, 63–67.

(4) Gopi, S.; Pius, A.; Thomas, S. Enhanced Adsorption of Crystal Violet by Synthesized and Characterized Chitin Nano Whiskers from Shrimp Shell. J. Water Process Eng. 2016, 14, 1–8.

(5) Wu, J.; Gao, H.; Yao, S.; Chen, L.; Gao, Y.; Zhang, H. Degradation of Crystal Violet by Catalytic Ozonation Using Fe/Activated Carbon Catalyst. Sep. Purif. Technol. 2015, 147, 179–185.
(6) Magureanu, M.; Piroi, D.; Gherendi, F.; Mandache, N. B.; Parvulescu, V. Decomposition of Methylen Blue in Water by Corona Discharges. *Plasma Chem. Plasma Process.* 2008, 28, 677–688.
(7) Kasprzyk-Hordern, B.; Ziólek, M.; Nawrocki, J. Catalytic Ozonation and Methods of Enhancing Molecular Oxygen Reactions in Water Treatment. *Appl. Catal., B* 2003, 46, 639–669.
(8) Ahmad, A.; Mohd-Setapar, S. H.; Chong, C. S.; Khatoon, A.; Wani, W. A.; Kumar, B.; Rafatullah, M. Recent Advances in New Generation Dye Removal Technologies: Novel Search for Approaches to Reprocess Wastewater. *RSC Adv.* 2015, 5, 30801–30818.
(9) Vakili, M.; Rafatullah, M.; Salamatnia, B.; Abdullah, A. Z.; Ibrahim, M. H.; Tan, K. B.; Gholami, Z.; Amouzgar, P. Application of Chitosan and Its Derivatives as Adsorbents for Dye Removal from Water and Wastewater: A Review. *Carbohydr. Polym.* 2014, 113, 115–130.
(10) Senthilkumar, S.; PORKODI, K. Heterogeneous Photocatalytic Decomposition of Crystal Violet in UV-Illuminated Sol-Gel Derived Nanocrystalline TiO2 Suspensions. *J. Colloid Interface Sci.* 2005, 288, 184–189.
(11) Zhang, H.; Duan, L.; Zhang, D. Decolorization of Methyl Orange by Ozonation in Combination with Ultrasonic Irradiation. *J. Hazard. Mater.* 2006, 138, 53–59.
(12) Soares, O. S. G. P.; Faria, P. C. C.; Orfão, J. J. M.; Pereira, M. F. R. Ozonation of Textile Effluents and Dye Solutions in the Presence of Activated Carbon under Continuous Operation. *Sep. Sci. Technol.* 2007, 42, 1477–1492.
(13) Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A. Adsorption of Methylene Blue on Low-Cost Adsorbents: A Review. *J. Hazard. Mater.* 2010, 177, 70–80.
(14) Sun, G.; Wheatley, W. B.; Worley, S. D. A New Cyclic N-Halamine Biocidal Polymer. *Ind. Eng. Chem. Res.* 1994, 33, 168–170.
(15) Sun, Y.; Sun, G. Novel Refreshable N-Halamine Polymeric Biocides: N-Chlorination of Aromatic Polymides. *Ind. Eng. Chem. Res.* 2004, 43, 5015–5020.
(16) Haham, H.; Natan, M.; Gutman, O.; Kolitz-Domb, M.; Banin, E.; Margel, S. Engineering of Superparamagnetic Core-Shell Iron Oxide/N-Chloramine Nanoparticles for Water Purification. *ACS Appl. Mater. Interfaces* 2016, 8, 18488–18495.
(17) Padmanabhuni, R. V.; Luo, J.; Cao, Z.; Sun, Y. Preparation and Characterization of N-Halamine-Based Antimicrobial Fillers. *Ind. Eng. Chem. Res.* 2012, 51, 5148–5156.
(18) Kocer, H. B.; Cercek, I.; Worley, S. D.; Broughton, R. M.; Huang, T. S. N-Halamine Copolymers for Use in Antimicrobial Paints. *ACS Appl. Mater. Interfaces* 2011, 3, 3189–3194.
(19) Natan, M.; Gutman, O.; Lavi, R.; Margel, S.; Banin, E. Killing Mechanism of Stable N-Halamine Cross-Linked Polymethacrylamide Nanoparticles That Selectively Target Bacteria. *ACS Nano* 2015, 9, 1175–1188.
(20) Dong, A.; Xue, M.; Lan, S.; Wang, Q.; Zhao, Y.; Wang, Y.; Zhang, Y.; Gao, G.; Liu, F.; Harnoode, C. Bactericidal Evaluation of N-Halamine-Functionalized Silica Nanoparticles Based on Barbatic Acid. *Colloids Surf., B* 2014, 113, 450–457.
(21) Gutman, O.; Natan, M.; Banin, E.; Margel, S. Characterization and Antibacterial Properties of N-Halamine-Derivatized Cross-Linked Polymethacrylamide Nanoparticles. *Biomaterials* 2014, 35, 5079–5087.
(22) Baruch-Sharon, S.; Margel, S. Preparation and Characterization of Core-Shell Polystyrene/Polychloromethylstyrlyene and Hollow Polychloromethylstyryene Micrometer-Sized Particles of Narrow-Size Distribution. *Colloid Polym. Sci.* 2009, 287, 859–869.
(23) Brelter, S.; Brelter, U.; Margel, S. Engineering of New Spiropyrany Photochromic Fluorescent Polymeric Nanoparticles of Narrow Size Distribution by Emulsion Polymerization Process. *Eur. Polym. J.* 2017, 89, 13–22.
(24) Sponarova, D.; Hork, D. Poly(N,N-Diethylacrylamide) Microspheres by Dispersion Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* 2008, 46, 6263–6271.
(25) Gelber, C.; Cohen, S.; Natan, M.; Banin, E.; Kolitz-Domb, M.; Margel, S. Engineering of New Methylstyrene Farmin Vinlyc Monomer and Crosslinked Poly(Methylstyrene Farmin) Nanoparticles of Narrow Size Distribution for Antibacterial and Antibiofilm Applications. *Polymer* 2016, 100, 95–101.
(26) Askinadze, N.; Gluz, E.; Ziv, O.; Mirzali, D. M.; Margel, S. Engineering of New Crosslinked Functional PEG Micrometer-Sized Particles of Narrow Size Distribution for Enzyme Immobilization. *Polymer* 2013, 54, 2926–2934.
(27) Boguslavsky, L.; Baruch, S.; Margel, S. Synthesis and Characterization of Polycrylonitrile Nanoparticles by Dispersion/Emulsion Polymerization Process. *J. Colloid Interface Sci.* 2005, 289, 71–85.
(28) Horák, D. Effect of Reaction Parameters on the Particle Size in the Dispersion Polymerization of 2-Hydroxyethyl Methacrylate. *J. Polym. Sci., Part A: Polym. Chem.* 1999, 37, 3785–3792.
(29) Steinmetz, H. P.; Rudnick-Glick, S.; Natan, M.; Banin, E.; Margel, S. Graft Polymerization of Stryyl Bisphosphonate Monomer onto Polypyrrole Films Study on Inhibition of Biofilm Formation. *Colloids Surf., B* 2016, 147, 300–306.
(30) Muratov, D. S.; Kuznetsov, D. V.; Il’nykh, I. A.; Mazov, I. N.; Stepashkin, A. A.; Tcherdyntsev, V. V. Thermal Conductivity of Polypropylene Filled with Inorganic Particles. *J. Alloys Compd.* 2014, 586, 5451.
(31) Lin, S. Y.; Chen, K. S.; Liang, R. C. Thermal Micro ATR/FT-IR Spectroscopic System for Quantitative Study of the Molecular Structure of Poly(N-Isopropylacrylamide) in Water. *Polymer* 1999, 40, 2619–2624.
(32) Hasik, M.; Bernasik, A.; Drelinkiewicz, A.; Kowalski, K.; Wendt, E.; Camra, J. XPS Studies of Nitrogen-Containing Conjugated Polymers-Palladium Systems. *Surf. Sci.* 2002, 507–510, 916–921.
(33) Haijpour, M. J.; Fromm, K. M.; Ashkarran, A. A.; De Aberasturi, D. J.; De Laramendi, I. R.; Rojo, T.; Serpooshan, V.; Parak, W. J.; Mahmoudi, M. Antibacterial Properties of Nanoparticles. *Trends Biotechnol.* 2012, 30, 499–511.
(34) Bouaïla, C.; Samar, M. E. H.; Ismail, F. Degradation of Methyl Violet 6B Dye by the Fenton Process. *Desalinization* 2010, 254, 35–41.
(35) Comparelli, R.; Fanizza, E.; Curri, M. L.; Gozzi, P. D.; Mascaro, G.; Passino, R.; Agostiano, A. Photocatalytic Degradation of Azo Dyes by Organic-Capped Anatase TiO2 Nanocrystals Immobilized onto Substrates. *Appl. Catal., B* 2005, 55, 81–91.
(36) Szpyrkowicz, L.; Juzzolino, C.; Kaul, S. N. A Comparative Study on Oxidation of Disperse Dyes by Electrochemical Process, Oxone, Hypochlorite and Fenton Reagent. *Water Res.* 2001, 35, 2129–2136.
(37) Hisaindee, S.; Meetani, M. A.; Rauf, M. A. Application of LC-MS to the Analysis of Advanced Oxidation Process (AOP) Degradation of Dye Products and Reaction Mechanisms. *TrAC, Trends Anal. Chem.* 2013, 49, 31–44.
(38) Jonathan, N. The Infrared and Raman Spectra and Structure of Acrylamide. *J. Mol. Spectrosc.* 1961, 6, 205–214.
(39) Gebicki, J. M.; Guille, J. Spectrophotometric and High-Performance Chromatographic Assays of Hydroperoxides by the Iodometric Technique. *Anal. Biochem.* 1989, 176, 360–364.
(40) Hicks, M.; Gebicki, J. M. A Spectrophotometric Method for the Determination of Lipid Hydroperoxides. *Anal. Biochem.* 1979, 99, 249–253.
(41) Van Deyne, A.; De Geyter, N.; Leys, C.; Morent, R. Influence of Water Vapor Addition on the Surface Modification of Polyethylene in an Argon Dielectric Barrier Discharge. *Plasma Processes Polym.* 2014, 11, 117–125.