

Research Article

Optical Active Thermal Stable Nanocomposites Using Polybutadiene-Based Polyurethane and Graphene Quantum Dot-MnO₂

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Synthesis and characterization of new polybutadiene-based polyurethane, graphene quantum dot- MnO_2 nanoparticles, and relative nanocomposites were set as the aim of current artwork. For this purpose, a one-pot polymerization approach was employed in preparation of polyurethane through the reaction of amine polyol and toluene diisocyanate (TDI) in presence of DBTDL catalyst. Nanocomposites were synthesized using 1 to 3 incorporation percent of graphene quantum dot- MnO_2 nanoparticles in polymer matrix. ¹H-NMR and FT-IR spectroscopies confirmed successful synthesis of reaction products including graphene quantum dot- MnO_2 , polyurethane, and nanocomposites. UV-vis and PL spectrophotometry techniques were applied for achieving optical information of samples. Optical properties of nanocomposites were reserved properly with no great quenching. Thermal stabilities, degradation rates, and thermal characteristics of polyurethane and nanocomposites were investigated using TGA/DTG and DSC analysis. Thermal stability showed direct relationship to nanoparticle content, and 3%wt nanocomposite showed improved thermal behaviour in comparison with pure PU. SEM, XRD, and AFM techniques proved successful nanocomposite synthesis with detecting nanoparticle species and fine nanoparticle dispersion with improved topographic and morphologic characteristics making GQD-MnO₂ polyurethane nanocomposites a good candidate for using in optical active and thermal stable coatings.

1. Introduction

At a time when socioenvironmental problems of polluting industries are the focus of legislators, the general trend is toward the production of new products from recycled materials, especially waste materials. In the case of polybutadiene, because of most usage in tire production in crosslinked form with sulfur or carbon dioxide, it does not seem so reasonable to pay attention on polybutadiene recycling, at least until recognition of successful separation approaches. However, crude polybutadiene itself faced some issues of processability like high molecular weight, high viscosity, low solubility, and high molding that can be solved for usage in wide speared areas with chain modification [1–4].

Based on a common belief in green chemistry, it is much more beneficial to produce high-performance polymers form existing low-use ones than new starting monomers. With this respect, chemical modification of polybutadiene chain could make possible goals like raising polymer applications, introducing high-performance polymers, and preventing overproduction of new polymers with optimistic perspective to polybutadiene recycling [5, 6].

Double-bond scission of polybutadiene chain usually occurs through chain oxidation using hydrogen peroxide, metachloroperbenzoic acid, and dimethyl dioxirane. The molecular weight could be engineered by peracid/double-bond unit ratio [7, 8]. Carbonyl functionalized polybutadiene derived from chain cutting down process is an attractive procedure for polyurea and polyurethane synthesis [9, 10].

A quantum dot is a zero-dimension material in nanoscale that is rewarded with unique optical properties consequenced by presence of some electrons captured in divided



FIGURE 1: Product picture. (a) GQD solution, (b) GQD powder, and (c) GQD-MnO₂.

energy levels [11]. First PbS quantum dot synthesis process was developed 2000 years ago using natural and low-cost compounds of PbO, $Ca(OH)_2$, and water that Romans and Greeks benefited from these products in makeup and hair colors. Quantum dot particle size controlling became one of the oldest and most frequent approaches in glass color rein. Also, CdS and CdSe were employed in addition of red-yellow paint in silica glass production [12]. Unparalleled properties like thermal conductivity, fluorescent, high surface ratio, low cytotoxicity and biocompatibility, chemical/ thermal stability, and nanoparticle size adjustable properties expanded the applications of graphene quantum dots (GQDs) [13].

It is possible to band gap engineering by alloying quantum dot as well as doping, without any change in particle size. Variety in metal count multiplicity or alloying compound ratio can affect optoelectronic properties of quantum dot. Several intermediate metals such as Ag, Hg, Co, Cu, Cr, Mn, Fe, Ti, Zn, and Cd have been reported in alloying quantum dots so far [14–16].

In current work, in the following of our previous reports [17, 18], it is decided to investigate the incorporation of MnO_2 alloyed graphene quantum dot in a new class of polybutadiene-based polyurethane nanocomposites by the foreword of the novel perspective to apply the designed optical active nanocomposites that may derive from low-use polymers.

2. Experimental Details

2.1. Materials. Previous reported approaches were used in telechelic amine polyol (Am, functionality = 4) synthesis explaining the oxidative degradation of polybutadiene chain [17]. Toluene diisocyanate (TDI, 174.2 g/mol molecular weight and 48%wt of NCO functional group content), dibutyltin dilaurate (DBTDL), citric acid, and sodium hydroxide (NaOH) were all purchased from Merck (Germany). Manganese dioxide (MnO₂) was supplied commercially. All solvents were completely dried and cleaned from impurities by rotary distillation and using molecular sieve before use.

2.2. Synthesis of $GQD-MnO_2$ Nanoparticles. At first, crystalline citric acid (2 g) was added into a 250 mL glass beaker and exposed to 200°C heat. The melting process and color change of citric acid began after 5 min heating. During 15 min, the solution color changed from colorless to yellow and orange at the end of the reaction. Graphene quantum dot (GQD) powder was achieved after dropwise solution neutralizing with 1 g/L NaOH solution and drying in room temperature.

At the second stage, synthesized GQD (0.5 g) was dissolved in distilled water (60 mL). MnO_2 powder (0.1 g) was added to the solution in ultrasonication situation. Compositing process lasted for 30 min, and the reaction mixture was centrifuged and washed several times with 50% waterethanol solvent. Graphene quantum dot alloyed manganese dioxide (GQD-MnO₂) nanoparticles were obtained after 1 day of putting the solution in 50°C vacuum oven. Figure 1 represents the product picture.

2.3. Synthesis of Polyurethane-GQD-MnO₂ Nanocomposite Films. Prepared amine polyol 0.25 mmol (0.3 g) and also GQD-MnO₂ (1, 2, and 3 percent related to polyol weight) were dissolved in dry dichloromethane solvent and exposed to ultrasonic radiation for 30 min. Reagent proportions are chosen how to have free isocyanate functional groups at the polymer tails as linking agents (e.g., 0.25 mmol of polyol and 1 mmol of diisocyanate bring forward 4 unreacted terminal isocyanate groups). TDI (150 μ L, 1 mmol) was dissolved in dry dichloromethane and added dropwise to the solution. DBTL (32 μ L, 55 μ mol) was injected at reflux term, and reaction mixture was stirred magnetically for 30 min in 60°C. The product was poured into a metal mold, and finally, PU-GQD-MnO₂ nanocomposite film synthesis was completed after 1 day drying in 50°C vacuum oven.

2.4. Characterization. ¹H-NMR instrument (Bruker DRX-300 AVANCE) was used to record spectra of sample solutions in CDCl₃ as solvent, applying TMS as internal standard and giving chemical shifts in ppm unit. A Fourier transform infrared spectrophotometer Thermo AVATAR (USA) was employed (400–4000 cm⁻¹) to investigate correct synthesis of nanoparticle and nanocomposite products. A thin layer of each sample solution in dichloromethane dry solvent was applied on KBr blank disc.

Solutions of samples in related solvent (distilled water or chloroform based on nature of the sample) were introduced to a cell of Camspec M350 Double Beam UV-vis instrument



FIGURE 2: (a) FT-IR spectra. (A) Citric acid, (B) GQD, and (C) GQD-MnO2. (b) FT-IR spectra of PU-GQD-MnO2.2.

(UK). Photoluminescence emissions of samples were recorded using 30-40 nm blue shift based on UV-vis absorbance in a Hitachi (Japan) PL instrument.

Thermogravimetric characteristics of polyurethane, nanoparticles, and nanocomposites were deliberated by a TGA/DTG technique (Perkin-Elmer Paris Diamond, USA), under N₂/O₂ atmosphere, temperature range of 0-800°C, and heating rate 7.5°C/min. Also, alternative thermal behaviour of polyurethane and nanocomposites in temperature domains of -100 to 250°C and heating rate of 10°C/ min was achieved using a TA SDT Q600 DSC instrument (USA).

Nanoparticle size, distribution, successful nanocomposite synthesis, morphology, and topographic investigations were performed using scanning electron microscopy (SEM, TESCAM MIRA III, Czech), X-ray diffraction (XRD, PHI-LIPS PW1730 Co., Netherlands), and atomic force microscopy (AFM, BRUKER ICON, USA) methods. XRD patterns were taken in 2θ ranging from 8° to 80° with scanning rate of 0.04°/s in room temperature (Cu Ka radiation, $\lambda = 1.54$



FIGURE 3: UV-vis spectra of synthesized GQD and GQD-MnO₂ nanoparticles.



FIGURE 4: UV-vis spectrum of PU-GQD-MnO2 nanocomposite.

Å). AFM pictures were taken in room temperature with applying gates of 1, 5, and $10 \,\mu$ m.

3. Results and Discussion

3.1. ¹*H*-*NMR Spectroscopy*. Correct synthesis of each sample toward polyurethane followed by ¹*H*-*NMR spectra* is shown in Figure S1 [17].

3.2. FT-IR Spectroscopy. FT-IR spectra are recorded for each sample for polyurethan synthesis approval (Figure S2) [17]. Stepwise nanoparticle synthesis followed by FT-IR spectra is shown in Figure 2. Stretching vibrations of acid and alcohol O-H groups of starting citric acid traced a strong absorption band at 3221 cm^{-1} in Figure 2(a), A that the twin-like shape of the absorbance could be considered as an approval to different nature of present OH groups. Acid C=O species are absorbed band at 1722 cm^{-1} for stretching



FIGURE 5: PL spectra of synthesized GQD and GQD-MnO₂ nanoparticle.



FIGURE 6: PL spectrum of PU-GQD-MnO₂ nanocomposite.

vibrations. Absorbances of stretching vibrations of CH_2 chain are recorded at 781 and 2926 cm⁻¹, and C-O bond stretching vibration shows a band at 1115 cm⁻¹ [19].

According to the synthesis process, some acid and alcohol groups of citric acid remain as active functional groups on GQD surface and edges; so, all absorption bands of citric acid also are emerged in GQD spectrum too (Figure 2(a), B). The difference is that the intensity of acid C=O group is reflowed because of acid decomposition and acid functional group content decrease. Absorption band at 1634 cm⁻¹ is related to the formation of benzene-like double-bond structure of GQD.

Based on GQD-MnO₂ spectrum, detected absorption band at 625 cm⁻¹ is related to vibrations in Mn-O bond that is a proof of MnO₂ presence in GQD-MnO₂. Besides, intensity of C-O stretching vibration absorption band at 1115 cm⁻¹ is declined, and a new absorption band appeared at 1041 cm⁻¹. Also, stretching vibration absorption band of O-H group is shifted to 3416 cm⁻¹. These observations can be recognized as successful interactions of MnO₂ with acid



FIGURE 7: PL TGA/DTG thermograms of PU-GQD-MnO2 nanocomposites (a) TGA and (b) DTG.

and alcohol groups of GQD surface that is leaded to relocations in absorption frequencies of C-O and O-H bonds (Figure 2(a), C) [15].

Successful PU-GQD-MnO₂ nanocomposite synthesis is proved in Figure 2(b) with identification of Mn-O bond absorption at 662 cm^{-1} . N-H moiety is accompanied in absorption bands at 3223 and 1545 cm^{-1} , respectively, for stretching and bending vibrations that the former is intensified with O-H absorptions of nanoparticles. Absorption bands at 1631 and 1701 cm⁻¹ are, respectively, observed for stretching vibrations of C=C and urethane C=O. Absorption bands at 1585 and 1454 cm⁻¹ are, respectively, attributed to vibrations of urethane linkage and aromatic ring breathing. C-N bonds are revealed absorption bands at 1385 cm⁻¹ for

International Journal of Polymer Science

Sample	Т ₀ (°С)	T ₁₀ (°C)	T ₅₀ (°C)	T_f (°C)
PU	186	208	382	471
PU-1GQD-MnO ₂	184	207	320	480
PU-3GQD-MnO ₂	210	243	427	485

TABLE 1: Thermal decomposition data of PU-GQD-MnO₂ nanocomposites.



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FIGURE 8: DSC thermograms of PU and PU-GQD-MnO₂.

stretching and 1184 and 1045 cm⁻¹ for bending vibrations that the prior is sharpened with C-O vibrations of the nano-particle in this area [17].

3.3. UV-vis Analysis. UV-vis spectra of two GQD and GQD-MnO₂ samples are shown in Figure 3. Based on GQD spectrum, an intense absorbance occurred at 200-300 nm range, with maximum intensity of 230 nm that is related to π - π * electron transfer in sp² carbons generated in GQD. Shoulder-type absorbance at 238 nm can be referred to the n- π * electron transfer in C=O bond of active acid groups on GQD surface. Another weak absorbance at 450-500 nm could be recorded because of the existence of GQD particles in nanometer range [12, 20].

Both mentioned absorbances are quenched and experienced a blue shift in GQD- MnO_2 in comparison with pristine GQD. Absorbance at 450 nm is completely broadened, and the shoulder-type peak is separated to two smaller peaks at 229 and 240 nm that refers to the difference between carbonyl group band gap energy in free state and interaction with MnO_2 . A quenching is observed in peak intensity by value of 77 a.u. according to the changes consequenced by metal entrance on quantum dot surface. Also, a blue shift of 15 nm is happened because of decrease in particle size of GQD- MnO_2 than GQD [11, 21].

Absorbance of π - π * electron transfer in C=C carbons, n- π * in C=O bonds of PU-GQD-MnO₂ nanocomposite, and nanoparticle interaction absorbance, respectively, are traced at 258, 300, and 486 nm. Blue shifts of 52, 71, and 36 nm than equivalent absorbances in pure GQD-MnO₂ are counted by extended band gaps of nanoparticles caused by successful nanoparticle interactions with PU. No quenching is visualized in absorbance intensities; so, the optical characteristics of nanoparticle are reserved during compositing process that is an optimistic perspective to use PU-GQD-MnO₂ in optical applications (Figure 4) [22].

3.4. PL Analysis. As it is shown in PL spectrum (Figure 5), GQD is emitted to two peaks of 390 and 490 nm with excitation wavelength of 250 nm. GQD-MnO₂ emission spectrum revealed a wavelength dependent behaviour that is contributed in 306 and 662 nm absorbances, respectively, for 250 and 550 nm excitations. Wavelength-dependent action of GQD-MnO₂ may be for the reason of differences in nanoparticle dimensions (length, width, and height) and also presence of various emission sites. PL spectrum intensities of GQD-MnO₂ are slightly quenched than pure GQD that brought forward well optical performance for GQD-MnO₂ nanoparticles [12, 23].

PL emission spectrum of PU-GQD-MnO₂ (Figure 6) is recorded with maximum wavelength value in 307-344 nm range with intensity of 10000 a.u., without any changes in wavelength and intensity in comparison with pure GQD- MnO_2 . No intensity decline and quenching are detected in nanocomposite PL spectrum; so, hopefully, the optical behaviour of nanocomposite is retained [24].

3.5. TGA/DTG Analysis. TGA/DTG thermograms of nanocomposites are plotted in Figure 7. Eight percent of GQD-MnO₂ nanoparticle weight is lost until 600°C. Several decomposition details in DTG thermogram reveal different segmentations and various interactions caused by alloying GQD with MnO₂. Based on thermograms of nanocomposites, two degradation stages are recorded after approximately



FIGURE 9: SEM micrographs of PU-GQD-MnO₂ nanocomposite. (a) ×5000, (b) ×50000, (c) ×100000, and (d) ×201000.

2 percent weight loss of moisture, impurities, or adsorbed solvents. First stage of hard segment degradation, 47 and 42 percent weight loss is happened at 308 and 338°C, respectively, in PU-1GQD-MnO₂ and PU-3GQD-MnO₂; with this respect, thermal stability of nanocomposites is raised by 7 and 37°C.

In the second stage related to decomposition of soft segment, PU-1GQD-MnO₂ and PU-3GQD-MnO₂ are degraded, respectively, 51 and 56 percent of the remained weight at 480 and 485°C. Final temperatures are postponed

for 9 and 14°C, that is, the positive effect of nanoparticle reinforcement on thermal properties of nanocomposites. Nanoparticle interactions with PU hard segments and formation of degradation sublevels in soft segments are the reason of delay in decomposition and thermal stability increment. Thermal decomposition data are summarized in Table 1 [25, 26].

3.6. DSC Analysis. DSC thermograms of PU and PU-GQD-MnO₂ are shown in Figure 8. First T_g related to mobility



FIGURE 10: XRD patterns. (a) PU, (b) GQD-MnO₂, and (c) PU-GQD-MnO₂ nanocomposite.

of polybutadiene soft segments is spotted at -73°C. Movement of PU hard segment is contributed in second T_g at 23°C with specific heat (Delta Cp^{*}) of 0.1 J/g*K. PU melting point is verified with enthalpy of 5.23 J/g at 88°C (T_m). Another endothermic event occurred at 199°C having enthalpy of 1.5 J/g that is attributed to hydrogen bond and interaction dissociation and also a hatch to PU degradation.

First and second T_g of PU-GQD-MnO₂ are observed at -75 and 18°C (0.03 J/g*K) meaning the nanoparticle interactions with hard segments are much stronger than with soft segments. Melting point is traced at 92°C with enthalpy of 13.72 J/g. The weak exothermic peak at 41°C could be attributed as tacticity and slight crystallization consequenced by nanoparticle compositing. Bond dissociation process began at 209°C with enthalpy of 6.06 J/g.

As consequences of nanoparticle reinforcement in PU matrix, melting point, melting enthalpy, dissociation temperature, and dissociation enthalpy are increased that led to rise in PU-GQD-MnO₂ thermal resistance. On one hand, soft and hard segment interactions with nanoparticle participated in polymer layer dividing, turbulence formation in polymer orientation, and increase in chain mobility [27]. On the other hand, free isocyanate group transforms to a softer segment by making interactions with nanoparticles that improves chain mobility. As a result, both PU-GQD-MnO₂ glass transition temperatures are declined in comparison with pristine PU. Melting point increase, dissociation temperature raise, and T_g decrease make nanocomposite utilization possible in wider thermal range [25].

3.7. SEM Analysis. SEM micrographs of PU-GQD-MnO₂ nanocomposite are imaged in Figure 9. Average detected nanoparticle size in polymer matrix calculation is 35.71 nm. GQD-MnO₂ nanoparticles make linkages to π bonds through physical interactions, and it is obvious to observe some agglomerations. However, it seems that making strong interactions by free isocyanate groups prevented thick assemblies. Finally, it can be resulted that nanoparticles

are distributed gracefully in PU matrix, and PU-GQD- MnO_2 nanocomposite synthesis is successful [28].

3.8. XRD Analysis. XRD patterns of PU and PU-GQD-MnO₂ nanocomposite are plotted in Figure 10. Amorphous character indicating broad peak is diffracted with maximum value of 20.41°. Single diffraction peak at 20.76° is characterized for slight crystallization consequenced by PU chain ordering and tacticity (Figure 10(a)) [26].

Amorphous diffraction of PU-GQD-MnO₂ is affected by interactions of PU chain with nanoparticle and is detected at 20.82° with some movement in comparison with pure PU pattern. Traced peaks at 28.62, 37.9, 41.06, 46.06, 56.56, 59.4, and 67.34° having d-spacing of 28.1, 21.4, 39.6, 17.7, 14.6, 14, and 12.5 nm are proved GQD-MnO₂ nanoparticle presence in polymer matrix and also PU-GQD-MnO₂ successful synthesis (Figures 10(b) and 10(c)) [23].

3.9. AFM Analysis. AFM images of topographic and morphologic investigations of PU and PU-GQD-MnO₂ surface are gathered in Figure 11. Hard and soft segments of polymer chain are, respectively, displayed as prominent and depression protrusions in 3-D scheme of film surfaces. Based on 2-D images, nanoparticles and soft segments are visualized darker, while macromolecules and hard segments are sound brighter. So, much darker parts in PU-GQD-MnO₂ 2-D image could be attributed to nanoparticle presence [29].

Statistic investigations of AFM data are calculated roughness mean of 146.7 and 33.33 nm, height mean of 1.96 μ m and 486.8 nm, and valley mean of -358.8 and -49.02 nm, respectively, for PU and PU-GQD-MnO₂. With this respect, maximum height for a random point of film surfaces is detected by values of 2.23 μ m and 124 nm by means of surface histogram. According to bearing plot, it can be resulted that more than 80 percent of surface height is arranged below 1.84 μ m and 453.74 nm, respectively, in PU and PU-GQD-MnO₂. Lowest surface height (R_q) using height profile is detected 177.9 and 42.65 nm, respectively, for PU and PU-GQD-MnO₂.



FIGURE 11: Continued.



FIGURE 11: AFM images of PU: (a) 3-D scheme, (c, e) 2-D images, (g) surface height histogram, (i) bearing plot, and (k) height profile; PU-GQD-MnO₂ nanocomposite: (b) 3-D scheme, (d, f) 2-D images, (h) surface height histogram, (j) bearing plot, and (l) height profile.

It can be resulted from all images and data surveying that synthesized PU is possessed surface thickness in micrometer range with segregated hard and soft segments. Also, GQD- MnO_2 particles in ranging nanoscale proved nanocomposite successful synthesis and homogenous distribution of nanoparticle in polymer matrix. Clutters and complexities of soft segments of polymer chain are declined, and thicknesses are decreased with exfoliations on surface consequenced by nanoparticle addition to PU matrix. These topographic results bring forward the utilization of nanocomposite application in optical coatings [30, 31].

4. Conclusion

At the beginning of this research, graphene quantum dot was successfully prepared by hydrothermal method and coprecipitation approach in order to have $GQD-MnO_2$

nanoparticle synthesis. GQD and GQD-MnO₂ nanoparticle accurate synthesis approved by FT-IR spectroscopy, and optical properties of nanoparticles were investigated with UV-vis and PL techniques. In the following, PU-GQD-MnO₂ nanocomposite was prepared through an in situ polymerization reaction of synthesized polyol and TDI diisocyanate in presence of different GQD-MnO2 nanoparticle percent. PU-GQD-MnO2 nanocomposite synthesis was confirmed using FT-IR technique. Also, it was resulted from UV-vis and PL analysis that nanocomposites excellently reserved their optical characteristics. Thermal property improvement of nanocomposites was observed using TGA/ DTG and DSC methods. Finally, SEM, XRD, and AFM investigations resulted satisfying nanocomposite synthesis, fine nanoparticle distribution, and morphologic and topographic property improvement in nanocomposites in comparison with pure PU.

Abbreviations

PB:	Polybutadiene
Am:	Telechelic amine polyol
PU:	Polyurethane
GQD:	Graphene quantum dot
GQD-MnO ₂ :	MnO ₂ alloyed graphene quantum dot
PU-GQD-MnO ₂ :	Nanocomposite of polyurethane with
	$GQD-MnO_2$ nanofiller
PU-1GQD-MnO ₂	Nanocomposites with, respectively, 1
and PU-3GQD-	and 3 weight percent GQD-MnO ₂
MnO ₂ :	nanoparticle in PU matrix
¹ H-NMR:	Proton nuclear magnetic resonance
	spectroscopy
FT-IR:	Fourier transform-infrared
	spectroscopy
UV-vis:	Ultraviolet-visible
	spectrophotometry
PL:	Photoluminescence spectroscopy
TGA/DTG:	Thermogravimetric and differential
	thermogravimetric analysis
DSC:	Differential scanning calorimetry
SEM:	Scanning electron microscopy
XRD:	X-ray diffractometer
AFM:	Atomic force microscopy.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Additional Points

Highlights. (i) Processability of pure polybutadiene can be solved for usage wider areas with chain modification. (ii) Alloying quantum dots with metals help to bring forward efficient optical properties. (iii) New MnO₂ alloyed graphene quantum dot particles were used in preparation of optical active nanocomposites. (iv) A quite fine version of optical active thermal stable polyurethane nanocomposites was successfully synthesized for probable use in optical coatings.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Zahra Rahmatpanah. The first draft of the manuscript was written by Zahra Rahmatpanah, and Mir Mohammad Alavi commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Supplementary Materials

Figure S1: ¹H-NMR spectra. (a) PB, (b) Ald, (c) Am, and (d) PU. Figure S2: FT-IR spectra. (a) PB, (b) Ald, (c) Am, and (d) PU. (*Supplementary Materials*)

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