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Visible-Light-Induced Anionic Photopolymerization of Ethyl-2-cyanoacrylate with Graphitic Carbon Nitride

Zehra Gul Coban, Cansu Esen, Baris Kumru, Azra Kocaarslan,* Yusuf Yagci, and Baris Kiskan*

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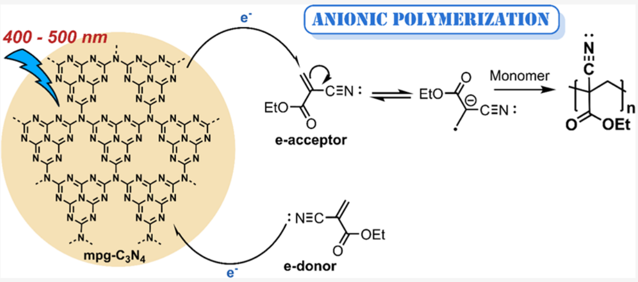
ABSTRACT: Two-dimensional (2D) materials have great potential in macromolecular synthesis, yet there are some areas that still need to be explored, such as anionic polymerization. In this study, we present the first example of photoinduced anionic polymerization of ethyl-2-cyanoacrylate (ECA) using 2D graphitic carbon nitride (g-C_3N_4) as an active photocatalyst responsive to visible light. Our results demonstrate that particularly the mesoporous structure of g-C_3N_4 can initiate polymerization through the generation of electron−hole pairs upon exposure to visible light. To have a better insight into mechanistic pathways, several experiments, including control experiments, are conducted. The obtained polymers and the synthesized g-C_3N_4 materials are characterized comprehensively by chromatographic, thermal, and spectroscopic techniques. Accordingly, this study demonstrates an innovative process that can offer several advantages over traditional polymerization methods, including the ability to initiate polymerization at ambient temperatures and achieve high polymerization rates.



INTRODUCTION

The utilization of light as an energy source offers several opportunities for conducting chemical reactions. Particularly, light-induced polymerization systems are of interest due to the reactions characterized by relatively low energy requirements and high reaction rates in contrast to traditional thermal methods. Moreover, these systems provide unique spatial and temporal control, enabling a wide range of applications, such as surface patterning, macromolecular architecture, smart curing, and designing bioactive macromolecules. Light irradiation can trigger free radical, ionic, oxidative, or even step-growth polymerizations[1−3] successfully. In general, the initiation step of photopolymerization not only dictates the polymerization mechanism but also can provide a control on polymerization to yield a polymer with a desired molecular weight and structure. Well-defined homo- and copolymers with narrowly dispersed molecular weight and structural and compositional homogeneity can generally be successfully achieved by living/controlled polymerizations or click chemistry methods.

In this regard, anionic polymerization is known as an inherently living system and can offer a high degree of control over the polymerization process. Certain types of versatile monomers have been utilized in anionic polymerizations; specifically, cyanoacrylates have the unique ability to undergo polymerization through either radical or anionic processes.[4,5] Although radical polymerization of these monomers is versatile, cyanoacrylate-type monomers are primarily known for their effectiveness in anionic polymerization. This is due to the electron-withdrawing effect of the −C≡N group present on these monomers, which enables them to form stable anionic species. As a result, they become sensitive to weak bases, even water, and polymerization initiates rapidly, unlike many other vinylic and acrylic monomers.[6−8] The rapid polymerization capability enables 2-cyanoacrylate (CA) to be widely used in many practical applications, for example, in adhesives,[9,10] dental fillings,[11] fingermarks,[12] and three-dimensional (3D) printing.[13] Furthermore, due to the biodegradability of some CA-based polymers, it can be used in drug delivery[14] and surgical glues.[15,16] While the research on conventional CA monomers has extensively focused on anionic polymerizations with different initiators,[17] there are relatively few reports on light-induced anionic photopolymerization.[18] Some early reports have indicated that certain coordination complexes and organometallic compounds can serve as initiators for anionic polymerization when exposed to ultraviolet (UV) light.[19−21] This process contains the generation of active initiating species through photolysis, which then give rise to anionic or neutral nucleophiles to drive the anionic polymerization. Moreover, initiator systems can be activated at longer wavelengths by utilizing radical photoinitiators, photosensi-

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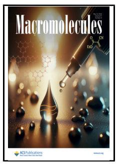

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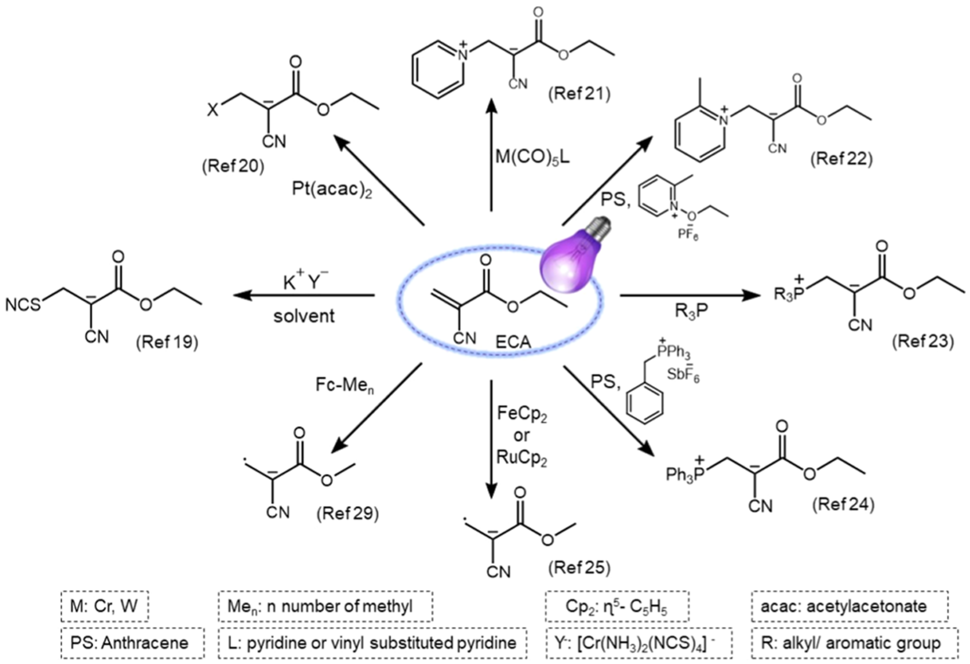
Scheme 1. Various Types of Initiation Systems for Ethyl-2-cyanoacrylate (ECA) Anionic Photopolymerization under Light Irradiation



tizers, and charge transfer complexes to enable polymerization (Scheme 1).[22−24]

In a similar manner, alkyl 2-cyanoacrylates (CAs) were successfully polymerized via an anionic mechanism using anionic species generated by irradiating group 8 metallocenes. Specifically, nonsubstituted ferrocenes and ruthenocenes were excited by light to promote electron transfer from the metallocenes to the CA monomer. This electron transfer resulted in the formation of a radical anion on CA, which then initiated the polymerization process[25−28] (Scheme 1). Furthermore, a recent study has shown that using electron-rich polymethyl ferrocene compounds is versatile for the light-induced anionic polymerization of different CA monomers.[29] Notably, although some mechanistic studies have been published, the initiation mechanism of metallocene-based systems still requires further clarification, as the fate of the radical within the initiating radical anion remains poorly understood.

Undoubtedly, investigating innovative methodologies for anionic polymerization remains as an attractive research topic. In particular, the utilization of light for discovering these innovative methods has critical significance because light can be an efficient tool when on-demand polymerization is required. Two-dimensional (2D) semiconducting materials show great potential in this context, as they have the ability to donate electrons by light, similar to metallocene systems. Therefore, it is possible that 2D semiconducting materials can initiate anionic polymerization through light activation. Moreover, most 2D semiconducting materials offer additional advantages such as reusability, efficiency, and simple reaction setups. Among these materials, graphitic carbon nitride (g-C_3N_4) has gained popularity in many photocatalytic reactions due to its ease of synthesis and more sustainable nature compared to metal-based semiconductors. Upon light exposure, these materials promote photoredox-induced pathways[30−33] where electron−hole pairs are generated as the electrons are donated simultaneously. The dislodged electron from the conduction band acts as a strong reducing agent, while the hole at the valence band acts as an oxidizer. Extensive research has been conducted on g-C_3N_4 and its counterpart mesoporous graphitic carbon nitride (mpg-C_3N_4) to explore their potential in photoinduced radical,[34] radical-promoted cationic polymerization,[35] controlled radical polymerization,[36,37] step-growth polymerization,[38] click reactions,[30] and oxidative polymerization.[39] Additionally, these materials offer opportunities not only to initiate polymerization processes but also to influence the mechanical and thermal properties of the final polymers.[40] In light of the context provided, it is worth exploiting the potential of 2D semiconducting materials, particularly mpg-C_3N_4, for light-induced anionic polymerization of alkyl 2-cyanoacrylates. Accordingly, catalytic amounts of g-C_3N_4 were dispersed in ethyl-2-cyanoacrylate (ECA) and then exposed to visible light, which resulted in poly(ethyl cyanoacrylate) (PECA) rapidly. Thus, this study presents a pioneering demonstration of the use of 2D semiconductors as photocatalysts in anionic polymerization.

■ EXPERIMENTAL SECTION

Materials. 2,4-Diamino-6-phenyl-1,3,5-triazine (97%, Sigma-Aldrich), 4-methyl-5-vinylthiazole (vTA, 97%, Sigma-Aldrich), cyanamide (Sigma-Aldrich), cyanuric acid (98%, Sigma-Aldrich), ethanol (99.5%, Kanto chemicals), NH_4HF_2 in water (4 M, 95%, Wako Chemicals), and SiO_2 particles in water (Ludox HS-40, Sigma-Aldrich) were used as purchased. Ethyl-2-cyanoacrylate (Henkel AG & Co. KGaA), hydroquinone (HQ, %99, Sigma-Aldrich), methanesulfonic acid (MSA, ≥99.0%, Sigma-Aldrich), acetonitrile (99.9%; Merck), and dichloromethane (Sigma-Aldrich) were also used in the experiments. Methyl methacrylate (MMA, 98%, Sigma-Aldrich) was purified by passing through a basic alumina column to remove the inhibitor and stored in a fridge.

Instrumentation. ^1H NMR spectra were recorded on a Bruker Ascend 400 NMR spectrometer using acetone-d_6 as a deuterated solvent. Gel permeation chromatography (GPC) measurements were performed on a TOSOH EcoSEC GPC system equipped with an autosampler system, a temperature-controlled pump, a column oven, a

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refractive index (RI) detector, a purge and a degasser unit, and a TSKgel superhZ2000, 4.6 mm ID × 15 cm × 2 cm column. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL/min at 40 °C. The refractive index detector was calibrated with polystyrene and poly(methyl methacrylate) standards having narrow molecular weight distributions. Data were analyzed by using Eco-SEC Analysis software. Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer FTIR Spectrum One spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Diamond DSC from −5 to 170 °C with a heating rate of 10 °C/min under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on a PerkinElmer Diamond TA/TGA with a heating rate of 10 °C/min under nitrogen flow (200 mL/min). Crystallographic measurements were accomplished by powder X-ray diffraction (PXRD) method on a benchtop Rigaku Miniflex diffractometer with a Cu-Kα radiation source operated at 30 kV and 10 mA. The acquisition angle ranged from 5 to 90° with 5°/min scan speed.

Synthesis of Organodispersible Carbon Nitride (CMp-vTA). CMp-vTA was synthesized according to the literature.[41] Overall, 1.30 g of cyanuric acid and 1.80 g of 2,4-diamino-6-phenyl-1,3,5-triazine were weighed and mixed in 50 mL of deionized water. The mixture was mixed overnight and the precipitate retrieved. Afterward, the precipitate was dried at 60 °C under a vacuum, and the mixture was transferred into a crucible, capped, and placed in an oven at 450 °C for 2 h with a heating rate of 2.3 °C/min under the protection of a nitrogen atmosphere. After cooling to room temperature, the yellow CMp powder was collected for further modification. 4-Methyl 5-vinylthiazole (vTA)-grafted CMp was obtained on post photo modification. Briefly, 300 mg of as-prepared CMp and 3 mL of vTA were added to a glass vial and sonicated for 15 min. The mixture was flushed with nitrogen for 20 min to remove the dissolved oxygen. Afterward, the mixture was put between two 50 W light-emitting diode (LED) daylight sources (20 cm apart from each other) for 3 h, and the obtained product CMp-vTA was washed with ethanol three times and dried under a vacuum at 60 °C overnight. (Surface area (Brunauer−Emmett−Teller (BET)): 12.33 m^2/g, pore volume: 0.105 cm^3/g.)

Synthesis of Graphitic Carbon Nitride (CM). Synthesis of graphitic carbon nitride using a cyanuric acid:melamine complex precursor was conducted according to the literature.[42] Overall, 10.0 g of cyanuric acid and 10.0 g of melamine were mixed with 200 mL of distilled water and shaken overnight to form a cyanuric acid−melamine supramolecular precursor. After centrifugation at 6000 rpm for 30 min, a precipitate was collected. The precipitate was dried overnight at 60 °C under a vacuum. The dried product was transferred into a capped crucible and put into a N_2-protected oven at 550 °C for 4 h, with a heating rate of 2.3 °C/min. The resulting yellow powder is denoted as CM, and it is well ground prior to use. (Surface area (BET): 16.54 m^2/g, pore volume: 0.117 cm^3/g.)

Synthesis of Mesoporous Graphitic Carbon Nitride (mpg-C_3N_4). A unity mass ratio of silica to cyanamide was used to synthesize mpg-C_3N_4. Cyanamide (20 g, Aldrich) was dissolved in a 40 wt % dispersion of 12 nm SiO_2 particles in water (50 g) with stirring at 353 K for about 3 h to evaporate the water. The resulting white powder was then heated at a rate of 2.3 K/min over 4 h to reach a temperature of 823 K and then held at this temperature for an additional 4 h in a nitrogen-protected oven. The resulting brown-yellow powder was stirred in 200 mL of 4 M NH_4HF_2 (95%, Wako Chemicals) for 2 h, followed by filtration and washing with 100 mL of H_2O and 50 mL of ethanol (99.5%, Kanto Chemicals). This washing cycle was repeated to completely remove the silica template. The powder was then stirred in 200 mL of H_2O for 2 h and then filtered and washed with H_2O and ethanol. Finally, the powders were dried at 393 K overnight. The yield of mpg-C_3N_4 was about 40% based on carbon content. (Surface area (BET): 165.55 m^2/g, pore volume: 0.372 cm^3/g.)

Glass Surface Treatment. All glass vials were freshly prepared. They were placed in a sulfuric acid solution (0.5 N) for overnight to get rid of SiOH on the surface of the glass.[29] Afterward, glass vials were washed with an excess amount of acetone to remove the acid residue from the surface and placed in acetone overnight. Then, the vials were dried in a vacuum oven at 40 °C overnight.

Photopolymerization. *Photopolymerization of Ethyl-2-cyanoacrylate by g-C_3N_4.* A mixture of ethyl-2-cyanoacrylate (ECA) (0.5 mL, 8.47 M) and g-C_3N_4 (10 mg) was placed in an acid-treated glass vial with a magnetic stirrer. The mixture was sonicated before the irradiation. The reaction mixture was irradiated in a Rayonet photochemical reactor equipped with six fluorescent light bulbs emitting light between 400 and 500 nm (λ_{max} = 450 nm) for 30 min. At the end of irradiation, the reaction mixture was added dropwise in 10-fold excess methanol (acidified methanol, %1 v/v methanesulfonic acid). The precipitated polymer was filtered and dried in a vacuum chamber for 24 h at ambient temperature. Subsequently, the reaction time was extended to 1 h (t_{photo}). It was observed that when the sample became viscous enough as a result of photopolymerization, the t_{photo} time stopped the Teflon stirring bar.[29] In order to analyze the molecular weights of the polymers, the irradiation of the reaction was kept for 30 min.

Polymerization of Ethyl-2-cyanoacrylate under Open Air. The reaction was conducted in a nontreated glass vial. An ECA monomer (0.5 mL) was placed in a vial and kept overnight in the open air under dark conditions. After 48 h, polymerization was completed.

Photoinduced Copolymer Formation of Ethyl-2-cyanoacrylate and Methyl Methacrylate. ECA (0.5 mL, 4.45 M), MMA (0.45 mL, 4.45 M) and mpg-C_3N_4 (10 mg) were placed in an acid-treated glass vial with a magnetic stirrer. The reaction mixture was irradiated in a Rayonet photochemical reactor with 6 fluorescent light bulbs emitting light between 400 and 500 nm (λ_{max} = 450 nm) for 30 min. After the reaction, the mixture was precipitated into 10-fold excess acidified methanol. The precipitated polymer was filtered and dried in a vacuum chamber for 24 h at ambient temperature.

Photopolymerization via Recycled g-C_3N_4. A mixture of ethyl-2-cyanoacrylate (ECA) (0.5 mL, 8.47 M) and g-C_3N_4 (10 mg) was placed in an acid-treated glass vial with a magnetic stirrer. The mixture was sonicated before the irradiation. The reaction mixture was irradiated in a Rayonet photochemical reactor equipped with 6 fluorescent light bulbs emitting light between 400 and 500 nm (λ_{max} = 450 nm) for 30 min. At the end of irradiation, dry dichloromethane (acidified DCM, %1 v/v methanesulfonic acid) was added to the reaction mixture. g-C_3N_4 was filtered and washed with dry DCM several times. The reaction mixture was added dropwise in 10-fold excess methanol (acidified methanol, %1 v/v methanesulfonic acid). The precipitated polymer and g-C_3N_4 were dried in a vacuum chamber for 24 h at ambient temperature. The same polymerization procedure was used in each cycle.

■ RESULTS AND DISCUSSION

It is well established that graphitic carbon nitride (g-C_3N_4) produces electron−holes under visible-light irradiation,[34] and charge separation efficiency and ingredients existing in the reaction media (i.e., cocatalysts, hole−electron scavengers) dictate a favored reaction pathway. For example, in most acrylate derivative monomers, g-C_3N_4 alone is insufficient to initiate direct radical formation on the monomer. However, by combining g-C_3N_4 with a coinitiator, such as diazonium salts and trialkyl amines, radicals can be effectively generated, resembling a type II photoinitiator system.[43] Consequently, effective light-induced radical polymerization with g-C_3N_4 requires certain types of hydrogen donors or electron-donating compounds. Therefore, this property of pure g-C_3N_4 brings to mind another possibility, such as the use of g-C_3N_4 as an electron source for anionic polymerization with alkyl cyanoacrylates. In order to test this hypothesis, initially, three different photocatalysts with different properties were synthesized, namely, mesoporous graphitic carbon nitride (mpg-C_3N_4) for a high surface area, organodispersible carbon nitride

(CMp-VTA) with superior dispersibility, and ordered carbon nitride made from a cyanuric acid:melamine complex (CM) for assessing the impact of structural order. The usual characterizations of these photocatalysts were conducted by Brunner–Emmet–Teller (BET) adsorption analysis, solid-state UV–vis spectra, photoluminescence spectra, FTIR spectra, powder X-ray diffraction (XRD) spectra, and scanning electron microscopy (SEM), as depicted in Figures S1–S4. Accordingly, all of the catalysts exhibit a relatively strong absorption over the 400 nm threshold. Moreover, the photocatalyst remained noninteracting with the solvent or the monomer according to the UV–vis analysis of the dispersion of mpg-C_3N_4 in the ECA and dichloromethane mixture (Figure S5).

It was well-documented that the reactivity of the ECA monomer toward water traces and residual alkaline compounds on glass vial surfaces can trigger premature anionic polymerization. Therefore, we conducted ECA polymerizations in glass vials treated with acid and dried under a high vacuum and temperature prior to photoinitiated anionic polymerization experiments. The efficiency of the acid treatments was controlled by placing small amounts of ECA in the treated vials and irradiating it under visible light. A polymerization was not observed after a certain period of time, demonstrating that the treated glass surfaces were free from contaminants. Accordingly, by following careful preparations and acid treatment procedures, we performed a series of experiments by varying the experimental conditions with ECA/mpg-C_3N_4, CM, or CMp-VTA to test the utility of these photocatalysts in anionic polymerization.

As a result of these experiments, carbon nitride materials demonstrated remarkable performance in photoinduced anionic polymerizations. Typically, light irradiation ceased once solidification became visibly evident within the polymerization vial (as depicted in Figure 1), and Table 1 summarizes the tested conditions and reaction times. Here, it should be noted that the conversion calculations were ambiguous; therefore, solidification times are given instead in the table.

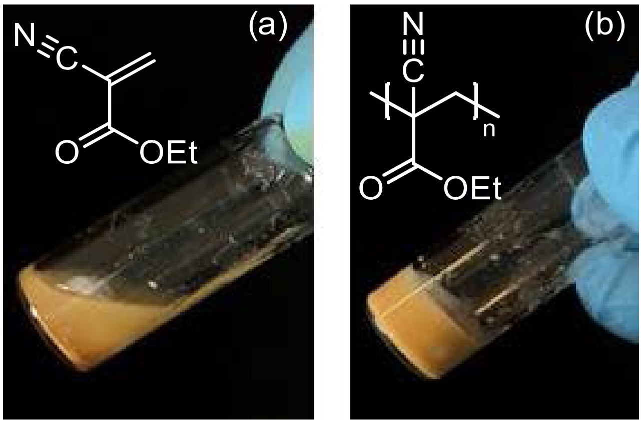


Figure 1. Images of the ECA/mpg-C_3N_4 mixture before (a) and after (b) light irradiation.

The results clearly indicated that doubling the amount of the photocatalyst led to significantly shorter solidification times under light irradiation (entry 1 vs 2). Moreover, the surface area of the photocatalyst had a profound impact on the polymerization process, and mpg-C_3N_4 exhibited noticeably superior performance compared to both CM and CMp-vTA.

Table 1. Photopolymerization Times (t_{photo}) for the ECA Monomer–Photocatalyst Pair[a]

entry	photocatalyst	amount of photocatalyst (g/L)	monomer	t_{photo} (min)[b]
1	mpg-C_3N_4	5	ECA	280
2	mpg-C_3N_4	10	ECA	180
3	mpg-C_3N_4	15	ECA	90
4	mpg-C_3N_4	20	ECA	60
5	mpg-C_3N_4	25	ECA	40
6	mpg- C_3N_4	20	MMA	n.s.[c]/n.p.[d]
7	CMp-vTA	20	ECA	n.s[c]
8	CM	20	ECA	120
9[e]	mpg-C_3N_4	20	ECA	n.s.[c]

[a] Conditions: [ECA] = 8.47 M with various photocatalysts under visible-light (400–500 nm) irradiation. [b] Determined as the solidification time at which the magnetic stirrer does not move. [c] n.s: no solidification. [d] n.p.: no polymerization. [e] Under dark conditions for 12 h.

The BET surface areas of mpg-C_3N_4, CM, and CMp-vTA used were ~166, 17, and 12 m^2/g, respectively. Notably, although polymerization occurred by CMp-vTA and a viscosity increase was observed, solidification was not observed after a certain time, indicating that polymerization yielded primarily low-molecular-weight polymers and oligomers. As a result, mpg-C_3N_4 was chosen as the photocatalyst for subsequent experiments. To demonstrate that the system relies on light induction, a control experiment in complete darkness was devised using the ECA/mpg-C_3N_4 mixture. In this blank experiment, no significant viscosity change was observed even after 12 h at room temperature. In addition to dark setting experiments, further investigations were conducted to exclude the potential influence of nucleophilic structures on the surface of mpg-C_3N_4. This was achieved by subjecting the photocatalyst to an acid treatment (HCl) to protonate any possible nucleophilic structures on the surface. The trials with the acid-treated mpg-C_3N_4 yielded results similar to the untreated counterpart and acted as a potent photocatalyst for ECA anionic polymerization. Consequently, these experiments provide compelling evidence that any surface initiation attributed to defect structures present on mpg-C_3N_4 is improbable and affirms that the initiation is driven by light induction. Upon photoexcitation at either sunlight or visible light (400–500 nm), the photocatalyst exhibits similar efficiency (Table S2). As established by earlier research, the polymerization mechanism of cyanoacrylate monomers is prone to follow either an anionic or a radical pathway depending on the initiation process.[4] In order to gain a better insight into the polymerization pathway, radical and anionic scavengers, namely, hydroquinone (HQ) and methanesulfonic acid (MSA), were separately added to the reaction mixtures. Table 2 shows that in the presence of hydroquinone, polymerization was not affected by the radical scavenger, and the polymer was formed with solidification, as shown in Table 2 entry 1. The molecular weight of the resulting poly(ethyl cyanoacrylate) was determined via gel permeation chromatography (GPC), with a value of 64.7 kDa and a typical low polydispersity of 1.1, consistent with anionic polymerizations (Figure S6). In addition, the structure of PECA was confirmed by FTIR and ^1H NMR spectroscopies (Figure S7). In the case of MSA addition, the presence of acid in the reaction medium acted as an inhibitor of formation of anionic species during the photopolymerization process. Although no viscosity change

Table 2. Photopolymerization[a] of ECA in the Presence of a Radical and an Anionic Scavenger

entry	hydroquinone (mol/L)	MSA (mol/L)	M_n (kDa)	Đ
1	2×10^{-2}		64.7	1.1
2		2.28	5	2.6

[a] Conditions: [ECA] = 8.47 M, 10 mg of mpg-C_3N_4 under visible-light (400−500 nm) irradiation. Irradiation time: 30 min. Viscosity was not observed, and the reaction solution was precipitated in acidified methanol (%1 v/v methanesulfonic acid) after 1 h.

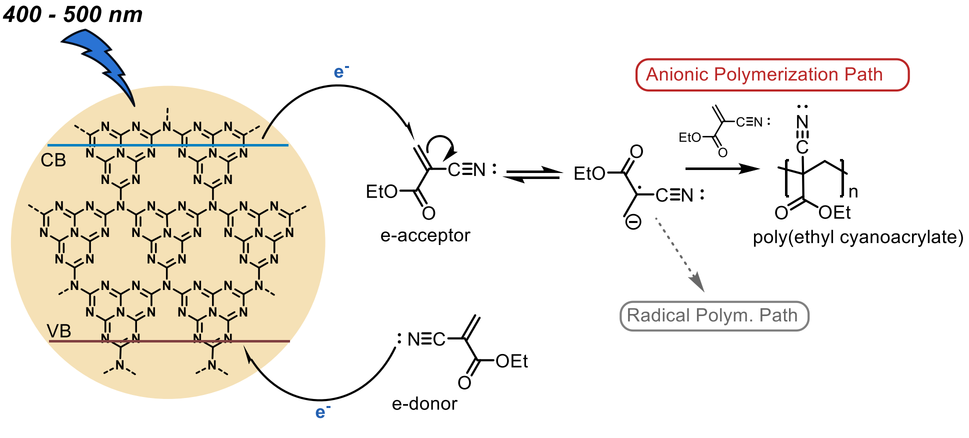
was observed, the solution was poured into cold methanol to analyze low-molecular-weight polymers via GPC. A minor amount of the precipitate was obtained, and the molecular weight (M_n) of this polymer was ca. 5 kDa with a 2.6 Đ. Furthermore, we introduced substantial amounts of MSA into the polymerization mixtures, adjusted the pH of the polymerization solutions to values between 2 and 4, and conducted similar experiments. In a parallel manner, no significant changes in viscosity were observed, and a small amount of the polymer (∼1% compared to the initial total monomer mass) precipitated in MeOH. These precipitated polymers exhibited Mn values ranging from 6 to 8 kDa and Đ values between 1.9 and 3.6, which are typical Đ values for the free radical process. The addition of acid clearly stopped the anionic mechanism but did not completely suppress the radical pathway. Evidently, these experiments revealed that the predominant pathway of the mpg-C_3N_4-catalyzed system is anionic, with a minor concurrent radical pathway.

Based on the results of our conducted experiments and the existing literature on carbon nitride chemistry, a plausible mechanistic explanation can be proposed for the observed polymerizations (Scheme 2). As previously discussed, carbon nitride systems release electrons from their conduction band, resulting in the simultaneous formation of electron−holes in the valence band of this semiconductor. These systems require electron-donating molecules, often named sacrificial agents, to maintain a continuous supply of electrons to the reaction medium. In the case of ECA/mpg-C_3N_4, the band-gap energy of mpg-C_3N_4 is large enough to generate electrons with sufficient reduction potential for ECA, which leads to the formation of radical anions on ECA. Concurrently, the nonbonding electron pair of the nitrile group of ECA donates electrons to the created holes in mpg-C_3N_4, effectively enabling the system to self-sustain a continuous supply of electrons. According to the previous reports related to metallocene-initiated anionic polymerizations, it is reasonable to infer that the generated radical anions on ECA can act as initiators for the polymerization process. On the other hand, the radical anion on ECA can also transfer an electron to the radical cation formed on the nitrile group easily, resulting in the production of neutral ECA for subsequent reactions. Actually, these electron transfer reactions reduce the number of radical species that are capable of initiating free radical polymerization. Notably, as our experiments have also shown, although it is minor, a radical pathway is inevitable in this proposed mechanism. Moreover, the overall mechanism provides a plausible explanation for the fate of the radical anions generated in a similar manner, which was discussed elusively in previous reports (refer to Scheme 1). Here, it should be noted that the band-gap energy of mpg-C_3N_4 possibly could not form electrons robust enough to trigger the reduction of methyl methacrylate (MMA) under the given experimental conditions. This reduction impotency of electrons on MMA could be the explanation for the unsuccessful polymerization of MMA (Table 1, entry 3).

Although the efficiency of light-induced electron transfer over mpg-C_3N_4 for reducing MMA species is limited to obtaining a homopolymer by an anionic pathway, we also explored the potential formation of copolymers with ECA. Undoubtedly, ECA and MMA exhibit markedly different reactivities in anionic polymerization, the possibility of a nucleophilic attack from a radical anion or an anion of ECA on MMA was still tested. Consequently, we synthesized PECA/PMMA polymers with varying ECA/MMA ratios through bulk polymerization in the presence of mpg-C_3N_4 exposed to UV light. Table 3 provides an overview of the resulting polymers, including their molecular weights and molecular weight distributions.

Differential scanning calorimetry analysis was also conducted in order to observe the thermal properties of the polymers. The glass-transition temperatures (T_g) of the homopolymer and the PECA/PMMA polymers are clearly traceable in Figure 2. The T_g of PECA obtained by mpg-C_3N_4 appears at around 136 °C, which is coherent with the reported range of 136−166 °C.[44] In contrast, the T_g of PECA

Scheme 2. Proposed Mechanism for Anionic Polymerization of Ethyl-2-cyanoacrylate in the Presence of mpg-C_3N_4 under Visible-Light Irradiation[a]



[a] CB and VB denote conduction and valence bands, respectively.

Table 3. Photopolymerization[a] of ECA with mpg-C_3N_4 (20 g/L) under Various Irradiation Times

entry	polymer	M_n[b] (kg/mol)	Đ
1	PECA	69	1.2
2	PECA/PMMA (1:1)	74.6	1.5
3[c]	PECA/PMMA (1:1)	64.3	1.4
4	PECA/PMMA (2:1)	73.4	1.1
5	PECA/PMMA (1:2)	71.4	1.6

[a] Conditions: [ECA] = 8.47 M, 10 mg of mpg-C_3N_4 under visible-light (400−500 nm) irradiation. Irradiation time: 30 min. The reaction time was deliberately chosen as 30 min due to the solution's rapid viscosity increase. [b] Molecular weight was determined by gel permeation chromatography (GPC) analysis. GPC samples were prepared with 0.1% MSA in tetrahydrofuran (THF) and measured by using a THF eluent and polystyrene calibration. [c] Polymerization was conducted in the presence of hydroquinone in dry CH_3CN.

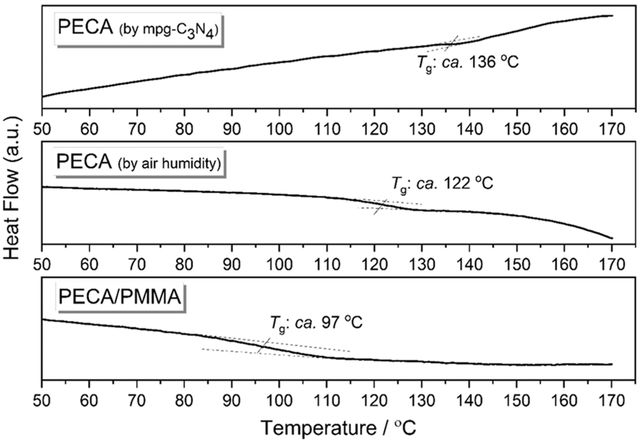


Figure 2. DSC traces of PECA synthesized with mpg-C_3N_4, PECA synthesized by air humidity, and PECA/PMMA (ECA/MMA, as 1:2 mol ratio).

synthesized under air humidity is observed at 122 °C. Moreover, furthermore, with the introduction of MMA content into the polymer, the T_g decreases to 97 °C for the ECA/MMA ratio of 2:1. The DSC analysis demonstrates only a single T_g, indicating the absence of a block copolymer or separate polymers. Both DSC and NMR results suggest a certain degree of copolymer formation; however, the synthesis experiments revealed that the polymer formation yields were so low. Only minor amounts of polymers could be obtained after precipitation in MeOH. Therefore, the low yield could be considered as an indication of the radical route for the formation of a copolymer, which is a minor path.

Further, a photocatalyst recyclability test was performed up to three times (Table S2). GPC results show that after the third cycle of photopolymerization, the photocatalyst loses the ability to control polymerization. The FTIR spectrum of the recycled photocatalyst shows the carbonyl peak (1747 cm^{-1}) of the PECA polymer remaining from the previous cycle (Figure S10). We believe that trapped PECA inside the pores of the photocatalyst inhibits efficient electron migration from the surface of the pores to the monomer. As shown in Figure 3, even after multiple cycles of photopolymerization, the mesoporous compound maintains its structural integrity without significant changes. Additionally, the XRD spectra provide valuable insights into the presence of any amorphous structures adhering to the photocatalyst's surface. Notably, the major peaks at 13.02 and 27.49° exhibit only minimal shifts, suggesting the absence of surface-initiated or attached polymers within the detection limits of XRD.

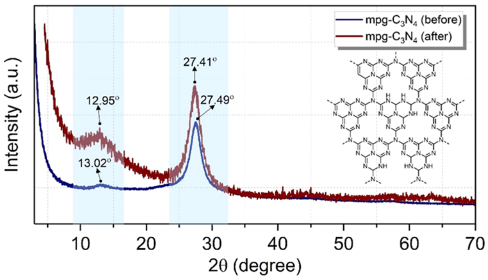


Figure 3. X-ray spectra of mpg-C_3N_4 taken before (blue line) and after (red line) its utilization in polymerization.

TGA and derivative thermogravimetry (DTG) studies provide valuable insights into the thermal stability and degradation behavior of the formed polymers. Air-polymerized ECA was used as a reference homopolymer to comparatively examine a thermal characteristic of the photopolymerized sample (Figure 4). Both the air-polymerized and photopolymerized ECA homopolymers exhibit weight loss, initiated ($T_{5\%}$) at approximately 195 and 213 °C, with complete degradation observed after 275 °C. The maximum degradation temperature for air-polymerized ECA is 236 °C; however, photopolymerized ECA shows two values at 237 and 261 °C. Moreover, the photopolymerized sample revealed a residual char of approximately 3% at 500 °C, in contrast to the air-polymerized sample, which underwent complete evaporation at the same temperature. This enhanced char formation observed in the photopolymerized sample can be attributed to the presence of residues of carbon nitride and the higher molecular weight characteristic of the photopolymerized sample.

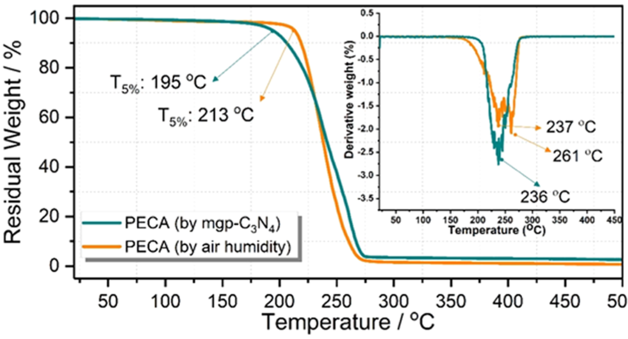


Figure 4. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of PECA synthesized with mpg-C_3N_4 (green line) and PECA synthesized by air humidity (orange line) from 30 to 500 °C with a heating rate of 10 °C/min under nitrogen flow.

■ CONCLUSIONS

This study showcases the successful application of two-dimensional semiconducting graphitic carbon nitride (g-C_3N_4) in anionic photopolymerization. Through a series of carefully designed experiments, we gained a better insight into possible mechanistic pathways. Accordingly, the proposed mechanism involves the liberation of electrons from mpg-C_3N_4 upon irradiation, which reduces the ECA monomer, forming a radical anion as the initiating species. In addition, the generated electron−hole on mpg-C_3N_4 captures electrons from the nitrile group of ECA. In this way, continuous electron supply is provided to the system by the monomer itself. Concomitantly, the redox between a radical anion and a cation forms anionic and neutral ECA. It was expected that these anionic species initiate the polymerization besides radical anions. While our initial expectation was that the anionic species would predominantly initiate polymerization, our experiments unveiled that the photoredox pathway also facilitates a minor radical pathway for photopolymerization. Furthermore, copolymerization attempts by combining ECA with methyl methacrylate (MMA) were also performed, and a series of experiments revealed the formation of some copolymers. However, it should be mentioned that the yields were low, suggesting that the incorporation of MMA is likely facilitated by a radical pathway and copolymer formation is sluggish. In conclusion, this study not only expands our understanding of anionic photopolymerization with semiconducting materials but also can trigger further research in the field of carbon nitride/anionic polymerization chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c02425.

Experimental Section and photocatalyst characterization and polymer characterization (PDF)

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Author Contributions

The experimental part was completed by Z.G.C. Synthesis and characterization of photocatalysts were completed by C.E. and B.K. This manuscript was written through the contributions of A.K. and B.K. This project was supervised by A.K. and Y.Y.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

ECA, ethylcyanoacrylate; PECA, poly(ethyl-2-cyanoacrylate); g-C_3N_4, graphitic carbon nitride; mpg-C_3N_4, mesoporous graphitic carbon nitride; CM, carbon nitride made from cyanuric acid−melamine complex; CMp-VTA, vinyl thiazole postmodified organodispersible carbon nitride

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