


Article

Polymerization Initiated by Graphite Intercalation Compounds Revisited: One-Pot Synthesis of Amphiphilic Pentablock Copolymers [†]

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[†] This paper is dedicated with best wishes to Professor Iliya Bl. Rashkov on his 80th birthday.

Abstract: This study reports the first attempt to employ a potassium–graphite intercalation compound (KC₂₄) as an initiator for the one-pot synthesis of a multi-block copolymer. The results obtained show that KC₂₄ successfully initiated the copolymerization, leading to a copolymer consisting of poly(styrene), poly(methyl methacrylate) and poly(ethylene oxide) blocks. When all three comonomers were introduced simultaneously or in a specific sequence, the resulting copolymers had molecular masses in the range between 170,000 Da and 280,000 Da. Their composition was investigated by size-exclusion chromatography with triple detection (dRI/UV/IR) and ¹H-NMR. The analyses indicated that all copolymers were enriched in methyl methacrylate (50–66 mol%) despite the fact that the comonomers were added in equimolar amounts. Due to the layered structure of the initiator, the polymerization took place in the graphite interlayer spaces and lead to extensive delamination, indicating at the potential to produce in situ graphite/copolymer composite materials.

Keywords: graphite intercalation compounds; anionic polymerization; block copolymers



Citation: Vladimirov, N.G.; Gitsov, I. Polymerization Initiated by Graphite Intercalation Compounds Revisited: One-Pot Synthesis of Amphiphilic Pentablock Copolymers. *Macromol* **2022**, *2*, 184–193. <https://doi.org/10.3390/macromol2020012>

Academic Editor: Ana María Díez-Pascual

Received: 10 March 2022

Accepted: 11 May 2022

Published: 14 May 2022

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1. Introduction

Recently, multi-component block copolymers have been enjoying increasing interest [1]. They offer a good model for the theoretical treatment of structure–property relationships in synthetic polymers [2,3]. In addition, the combination of building blocks with vastly different chemical compositions and behaviors yields promising macromolecular platforms for many applications in advanced technologies [4], combinatorial processes and in the biomedical field [5]. Among the various techniques used to produce these materials, the single-vessel one is particularly attractive due to desirable savings in time and the relative simplicity of the reaction setup, among other benefits [6]. Cationic [7], anionic [8], radical [9] and enzymatic [10] protocols have been employed. Despite the recent advances in polymerization techniques, the one-pot anionic synthesis of multiblock copolymers from vinyl and heterocyclic monomers is still a rare and challenging synthetic procedure [8]. Surprisingly, the graphite intercalation compounds (GICs) [11] and specifically those of the alkali metals have been oddly overlooked and rarely used as potential one-pot catalytic systems [12]. The potential benefits include, but are not limited to, the graphite availability, the well-established formation protocols of the GICs and the confirmed initiating ability for a broad array of monomers [12]. Because of their well-pronounced “sieve effect” [13], the GIC initiators would be able to selectively absorb monomers from the initial polymerization mixture and produce copolymers that would otherwise require a multi-stage copolymerization and/or additional chemical modifications. Indeed, some early publications have reported that a second stage GIC of potassium (KC₂₄) successfully initiated the copolymerization of vinyl and heterocyclic comonomers (π - and n -donors, respectively) [14,15]. The

GIC-induced synthesis of multi-block copolymers with complementary block properties has not been reported. To test this possibility, the first of its kind synthesis of an ABC-type block copolymer, initiated by GIC via one-pot copolymerization, is the main goal of this study. For the proof of principle, the initiator chosen was KC_{24} and the target product was a copolymer with poly(styrene) PSt, poly(methyl methacrylate) PMMA and poly(ethylene oxide) PEO blocks. Since the initiation and chain-growth reactions were expected to proceed between the graphene sheets of the initiator [12], the process would intrinsically lead to an extensive graphite delamination, which might be useful for the in situ formation of graphite (nano)composite materials with a tailor-made composition. The initial hypothesis is illustrated in Figure 1.

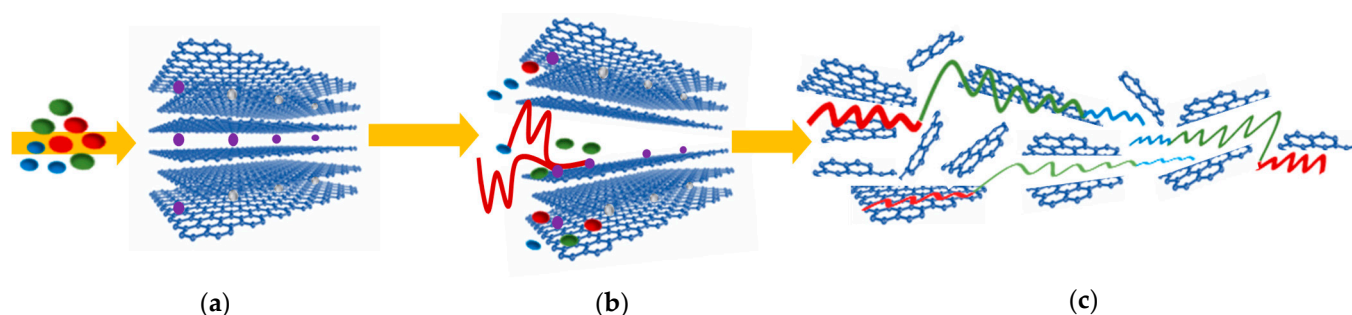


Figure 1. Tentative mechanism of the copolymerization process initiated by KC_{24} . (a) Monomer diffusion/absorption; (b) initiation/copolymerization; and (c) chain growth/GIC delamination. Red: styrene monomer/block; green: methyl methacrylate monomer/block; blue: ethylene oxide monomer/block; and purple: K-cation.

2. Materials and Methods

2.1. Materials

Graphite (Madagascar, flake size 100–125 μm), cyclohexane (CH), tetrahydrofuran (THF) p-xylene (pure, all from Fluka Chemie GmbH, Buchs, Switzerland) and ethanol (pure, Factory for Pure Chemicals, Vladaia, Bulgaria) were used as received. Styrene (St, 99%) and methyl methacrylate (MMA, 99%) were purchased from Fluka Chemie GmbH (Buchs, Switzerland), and dried over CaH_2 under vacuum. Ethylene oxide (EO, 98%, Neftochim, Burgas, Bulgaria) was dried by consecutive vacuum distillations over CaH_2 and n-butyl lithium.

2.2. Methods

The formation of the initiator, purification of the monomers, dosage of the reagents and polymerizations were carried out in vacuo (10^{-4} mm Hg) using all-glass apparatuses and ampoules equipped with breaking seals (see for example [16,17]). **Attention:** EO is a highly volatile, flammable and explosive liquid, which should be handled with extreme care during purification and kept at <-70 $^{\circ}\text{C}$ when torch sealed under vacuum.

2.2.1. Initiator Synthesis

KC_{24} was synthesized by Herold's method [18] with small modifications. Briefly, the graphite flakes were degassed over several hours in the synthesis vessel under stirring. Potassium was distilled in, forming a mirror, and the reaction temperature was gradually increased to 250 ± 1 $^{\circ}\text{C}$. Initially, the graphite turned golden bronze, indicating the formation of KC_8 , and then the color gradually changed to bright blue, signaling the transformation to KC_{24} . The mixture was kept under stirring while the temperature was let to gradually cool down. KC_{24} is stable over many years if stored in breaking-seal ampoules under vacuum, Figure S1.

2.2.2. Copolymerization

The copolymerizations were performed in bulk unless indicated otherwise. Typical quantities of the reagents were as follows: St—2 mL (1.82 g, 1.747×10^{-2} M), MMA—1.86 mL (1.7 g, 1.748×10^{-2} M), EO—0.88 mL (0.77 g, 1.748×10^{-2} M) and KC_{24} —1.9 g (5.81×10^{-3} M). In all cases, the initiator was introduced first with the monomers added at 0 °C either simultaneously or consecutively at an interval of 1 h each, and then the copolymerization mixture was slowly warmed up to 25 °C. The process was allowed to proceed for 27 h at 25 °C and was then quenched with degassed THF/HCl (trace). The products were dissolved in THF and the graphite particles were vacuum filtered and washed three times with THF portions of 5 mL each. Only small amounts (0.1–0.2 g) or traces from the initial amount of the graphite particles were recovered. The solvent was evaporated, yielding gray hard solids. The eventual homopolymers were removed by consecutive extractions with cyclohexane (40 °C, 48 h) for PSt (~10–17% of the isolated low-molecular-mass multimodal product containing MMA sequences, Figure S2) and ethanol/water (1/1 v/v) for PEO (~3–5% ill-defined copolymer, no PEO homopolymer recovered).

2.2.3. Polymer Characterization

The molecular mass of the copolymers was evaluated by size-exclusion chromatography (SEC). The analyses were performed in THF at 45 °C and at a flow rate of 0.8 mL/min. Two analytical SEC lines were employed: the first one consisted of a WISP 710B automatic injector, M510 pump, differential refractive detector R401, M440 UV detector (all from Waters, Co., Milford, MA, USA) and an infra-red (IR) detector Foxboro–Wilks Miran 1A. The separation was achieved across four ultra-Styragel columns (500, 10^3 , 10^4 and 10^5 Å, Waters, Co., Milford, MA, USA) calibrated with a set of 14 PSt standards (Waters Co.) in the molecular mass range between 1 kDa and 900 kDa. The second SEC line included a U6K universal injector, M510 pump, M410 differential refractive index detector and a M991 photo-diode array UV detector, PDA (all from Waters, Co., Milford, MA, USA). Analyses were carried out over three ultra-Styragel Linear columns (Waters, Co., Milford, MA, USA).

The chemical composition of the isolated ABC copolymers was examined using both SEC lines and by ^1H NMR analysis carried out on a 250 MHz Bruker DRX instrument (Bruker, Co. Billerica, MA, USA) in CDCl_3 at room temperature with tetramethylsilane (TMS) as an internal standard. The integral intensity of the aromatic protons (5H, 7.25–6.35 ppm), $-\text{CH}_2\text{CH}_2\text{O}-$ protons (4H, 3.64 ppm) and $-\text{C}(\text{CH}_3)-$ protons (3H, 1.3–0.6 ppm) was taken as a whole and then the relative content of the PSt, PEO and PMMA blocks was calculated, see the Supporting Information for details. In addition, the composition was determined from the area of the SEC peaks recorded by the PDA UV detector ($\lambda = 260$ nm) and the IR detector ($\lambda = 5.81 \mu\text{m}$, 1721 cm^{-1}), with calibration curves constructed with pure PSt (UV) and PMMA (IR) of similar molecular masses. The two techniques yielded similar data within $\pm 5\%$.

3. Results and Discussion

The copolymerization of the three comonomers (St, MMA and EO) showed all the characteristic features of previous polymerizations conducted with the GICs of the alkali metals. Upon monomer addition, the blue color of the initiator turned black, and the graphite flakes appeared to swell. As the polymerization progressed, the bulk mixtures gradually solidified and the stirring stopped after approximately 2 h (STEM 1 and 2, Table 1). The apparent viscosity of the p-xylene copolymerization mixture (STEM 3, Table 1) increased slightly, and the solution turned dark gray. For both the bulk and solution syntheses, the purified copolymers still had a gray color after the initiator filtration and extraction sequences. The yield dependence on the copolymerization conditions is presented in Table 1.

Table 1. Influence of the copolymerization conditions ¹ on the copolymer yields.

Product	M ² Addition Sequence	Temperature (°C)	Time (h)	Yield ³ (%)
STEM 1 ⁴	All	25	27	80
STEM 2 ⁴	St/MMA/EO	25	27	68
STEM 3 ⁵	St/EO/MMA	25	42	78

¹ For copolymerization conditions, see Section 2.2.2. ² M: monomer. ³ Apparent yield, determined after selective extraction of the copolymerization mixture, which still contains significant amounts of graphite (1.5–1.6 g, 79–84%).

⁴ Copolymerization in bulk. ⁵ Copolymerization in p-xylene, [M] = 1 mol/L.

The observed differences in the copolymer yields (averaged from three identical experiments) reflect the peculiar interactions of the three monomers with KC₂₄. A polymerization process, initiated by a GIC, proceeds in three stages—(1) diffusion of the monomer into the graphite interlayer spaces, (2) initiation + propagation + onset of the GIC delamination and (3) chain growth completion + full GIC delamination. Figure S3 shows a model copolymerization reaction performed with KC₂₄ made of highly oriented pyrolytic graphite (HOPG, Union Carbide, Houston, TX, USA). The changes in the GIC structure during stages two and three are clearly visible.

When all comonomers are added at once, their diffusion and polymerization would be controlled by their affinity to KC₂₄. A previous investigation [14] has established the following order of inclusion preference: St (π donor) \geq MMA (n - π donor) \gg EO (n -donor). Since no pure PSt, PMMA and PEO were isolated in measurable quantities, the most probable mechanism of the process is as follows: St was absorbed first into the GIC. There, it was transformed into an anion radical by electron transfer from the negatively charged graphenes and dimerized. The resulting di-anion added new St molecules and polymerization started. MMA entered next and was most likely initiated not by KC₂₄, but by the propagating PSt anions that were still fixed in the interlayer spaces. When this happened, further MMA molecules were preferentially added because the MMA anion cannot initiate/add another St monomer [19,20]. EO was very slow to penetrate between the graphene layers and only a small portion was incorporated either in the block copolymer or into the oligomer fractions extracted with the aqueous mixture (no pure PEO was found in the aqueous extraction fraction). It is highly likely that most of the unreacted EO was lost during the filtration and the evaporation of the extract mixtures under vacuum. Based on the assumed mechanism, the copolymer formed would have the following composition: PEO-*b*-PMMA-*b*-PSt-*b*-PMMA-*b*-PEO.

The copolymerization in p-xylene produced similarly high yields (STEM 3, Table 1), with the solvent probably acting as an additional space opener. The St/MMA/EO sequential addition in bulk (STEM 2, Table 1) produced the lowest yield, with EO evidently hampered to approach the active centers of the propagation immobilized in the interior of the GIC and screened by long PSt and PMMA segments.

SEC analyses of the copolymerization mixtures before and after selective extractions showed that the copolymers formed had a broad molecular mass distribution, Figures 2 and 3. The result is not surprising and is typical for the heterogeneous diffusion-driven polymerization processes initiated by GICs [14,15]. More importantly, the traces from all three detectors (dRI, UV and IR) appeared within the same elution window and followed the same monomodal pattern, Figures 2 and 3a. This result indicates that in all three addition modes, St, MMA and EO participated predominantly in a single copolymerization process with little to no homopolymerization (~13–22% multimodal copolymers and no measurable amounts of PMMA and PEO). It should be noted that the sequential additions mimic the order by which the monomers would be preferentially absorbed into KC₂₄. This order also facilitates the successful coininitiation, taking into account the well-known fact that oxyanions initiate MMA polymerization but do not initiate St polymerization. Indeed, in a separate experiment, when an EO/St/MMA addition sequence was experimented, the resulting polymer products had a bimodal molecular mass distribution with the later

eluting of a fraction enriched in MMA and a high molecular mass shoulder, showing stronger UV absorption (i.e., higher St content), Figure 3b.

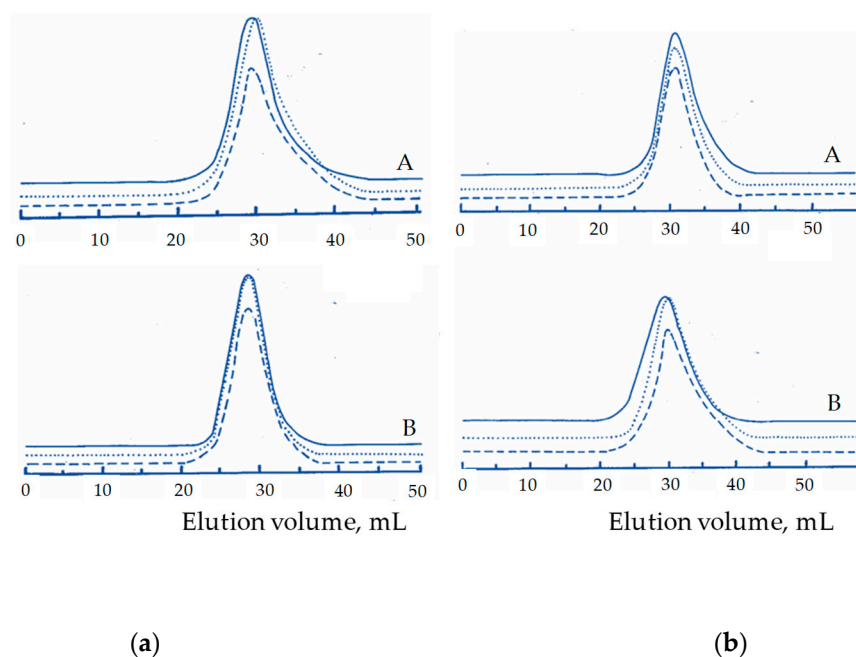


Figure 2. SEC eluograms of copolymers obtained after (a) simultaneous introduction of comonomers (STEM 1, Table 1) and (b) consecutive St/MMA/EO addition (STEM 2, Table 1). A—copolymerization mixture; B—copolymer isolated after two selective extractions. Detector signals: (—) dRI, (---) UV and (····) IR.

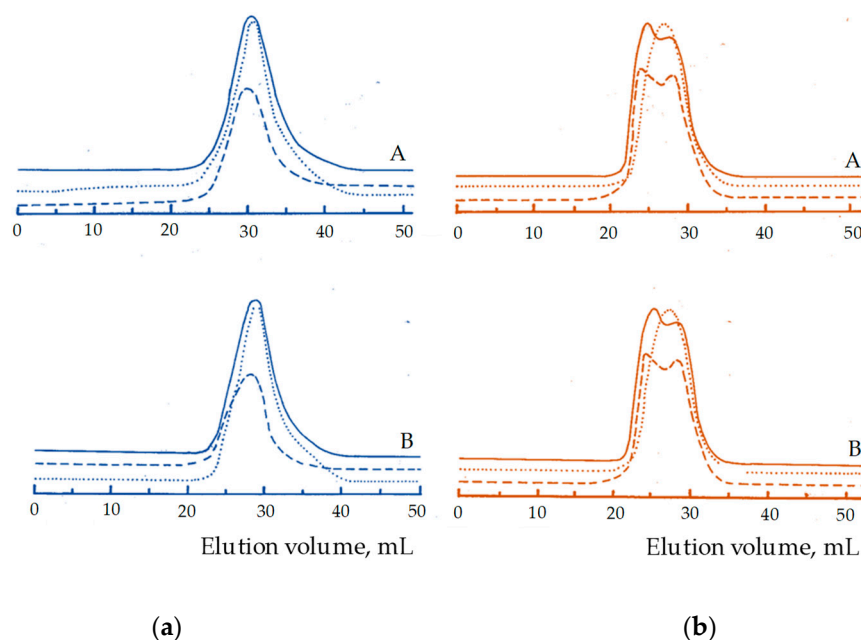


Figure 3. SEC eluograms of copolymers obtained after (a) consecutive St/MMA/EO addition in p-xylene (STEM 3, Table 1) and (b) consecutive EO/St/MMA addition in bulk. A—copolymerization mixture; B—copolymer isolated after two selective extractions. Detector signals: (—) dRI, (---) UV and (····) IR.

The scenario of the three homopolymers, having the same hydrodynamic volume and molecular mass distribution, co-eluting at the same time was proven to be highly unlikely by a 3D UV analysis of the purified copolymerization products, Figure 4.

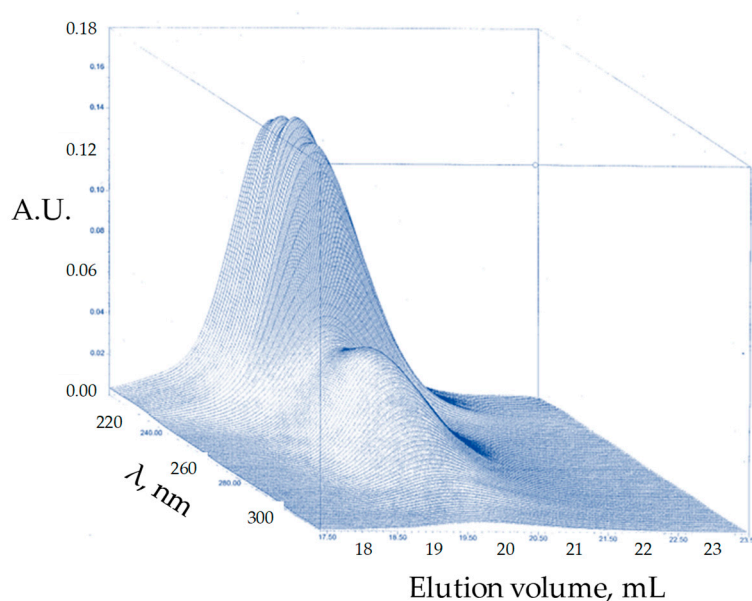


Figure 4. SEC eluogram of a copolymer obtained after simultaneous addition of comonomers (STEM 1, Table 1 and Figure 1a,b). UV PDA trace.

The three software-extracted UV spectra from the eluting polymer peak, taken at 19.12 mL, 19.4 mL (peak apex) and 20.47 mL (Figure 5a) were almost identical (Figure 5b). The absorption maximum at 260 nm with a small shoulder at 295 nm was caused by the St repeating units in the copolymer aligning not randomly, but in a block sequence [21]. The peak at 214 nm (Figure 5b) was due to the THF solvent, while the other two strong absorption maxima at 220.8 and 228 nm could probably be attributed to the MMA repeating units in the copolymer [22,23]. The existence of the EO blocks in the copolymers could not be detected by this method since PEO is UV transparent. The presence of EO repeating units is clearly visible in the ^1H NMR spectra of the purified copolymers, Figure 6.

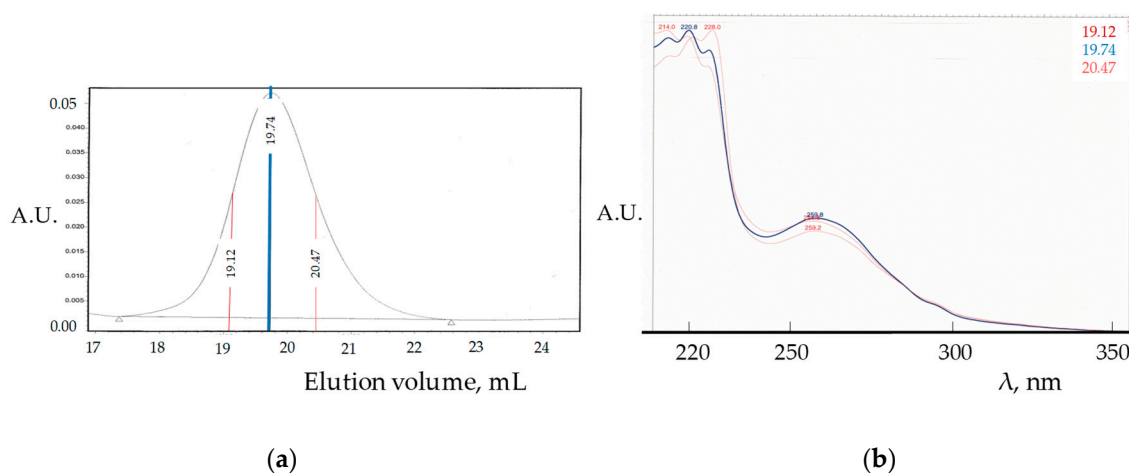


Figure 5. SEC eluogram of a copolymer obtained after simultaneous addition of comonomers (STEM 1, Table 1 and Figure 1a,b). (a) UV PDA trace at 260 nm; (b) overlaid UV spectra of fractions eluting at 19.12 mL, 19.4 mL and 20.47 mL.

Table 2. Molecular mass and composition of ABC terpolymers depending on mode of monomer addition.

Product	$M_w \times 10^3$ (SEC) ¹	Dispersity ² (Đ)	PMMA Microstructure mm/mr/rr	Molar Content ³ St/MMA/EO
STEM 1 ⁴	175	3.16	0.20/0.50/0.30	0.19/0.66/0.15
STEM 2 ⁴	279	5.90	0.16/0.52/0.32	0.30/0.50/0.20
STEM 3 ⁵	175	3.60	0.08/0.43/0.49	0.28/0.62/0.10

¹ Molecular mass determined by calibration with PSt standards. ² M_w/M_n determined by SEC. ³ Average values calculated with data from UV/IR SEC traces and NMR signal integration (see Supporting Information for details).

⁴ Copolymerization in bulk. ⁵ Copolymerization in p-xylene.

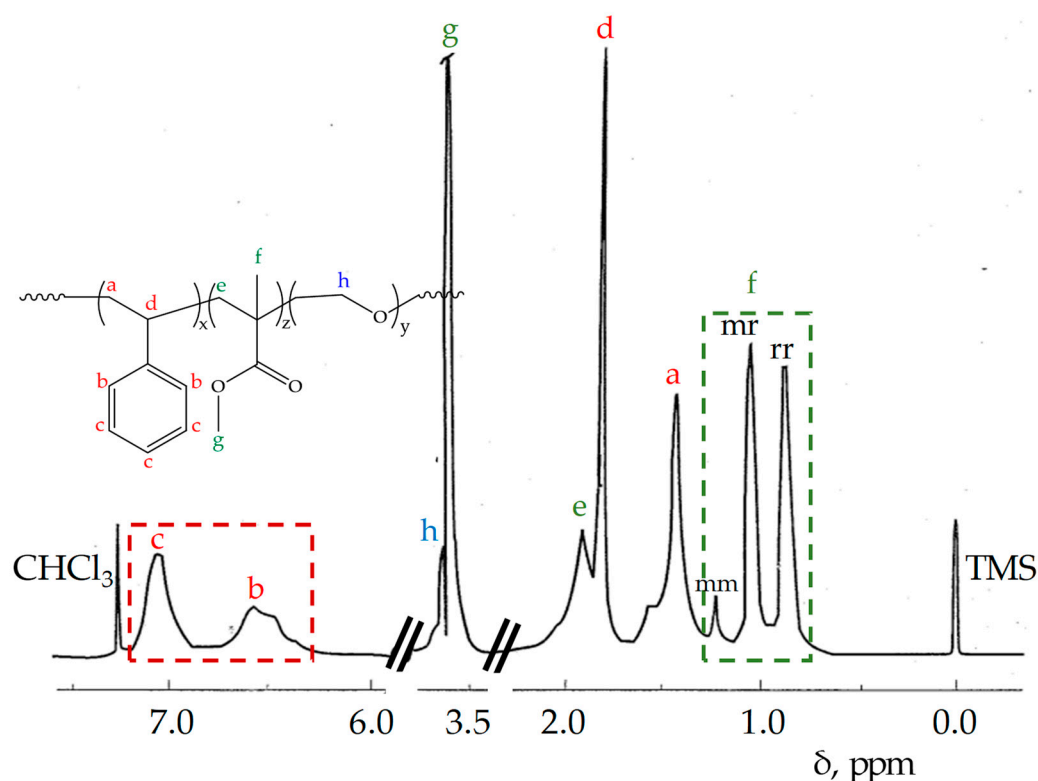


Figure 6. ^1H NMR spectrum of purified copolymer obtained after simultaneous addition of comonomers (STEM 1, Table 1 and Figure 1a,b). The integral intensity of the framed signals (red—aromatic protons, green—backbone methyl protons) and h (backbone methylene protons) was used for copolymer composition estimates (Table 2).

The existence of well-separated signals for the backbone $-\text{CH}_2-\text{CH}(\text{Ph})-$ and $-\text{CH}_2-\text{C}(\text{CH}_3)-$ groups of the St and MMA repeating units in the copolymers in distinction to their position in the ^1H NMR spectra of random St/MMA copolymers [24] could be interpreted as evidence for their arrangement in individual blocks (a, d and e, Figure 6).

The molecular masses of the isolated copolymers were rather high regardless of the comonomer mode of addition, the one with the St/MMA/EO sequence being the highest, Table 2. This shows that the initiator efficiency (f) was very low, taking into account the KC_{24} amounts used. The close resemblance of the molecular mass characteristics between the products obtained by the simultaneous introduction and sequential addition of the comonomers provides an additional insight into the probable copolymerization mechanism. At similar absorption tendencies between St and MMA, the inability of the MMA anions to initiate St polymerization [19,20] led to longer sequence of MMA repeating units (Molar Content, Table 2). The higher MMA content also indirectly hints at the pentablock character of the copolymerization product with two PMMA blocks present.

The disproportionally high MMA content compared to the St and EO repeating units was persistent across all NMR spectra. This result is to some extent surprising in view of an early paper reporting the formation of low yields of St-enriched St–MMA copolymers synthesized with KC₂₄ as initiator [25]. It should be noted, however, that that particular copolymerization was performed in dimethoxyethane, a solvent capable of solvating the K cation in the GIC. Another seemingly conspicuous result from the NMR analysis is that the isolated yields in all three series were significantly higher than those estimated by the ¹H NMR composition of the copolymers—80% vs. 37% (STEM 1); 68% vs. 54% (STEM 2); and 78% vs. 49% (STEM 3), Tables 1 and 2 and Figure 6. This discrepancy could possibly be explained by the fact that large portions of the GIC initiators remained embedded in the copolymers even after the precipitation/extraction sequence at which the oligomers and unreacted monomers were also removed.

The ¹H NMR spectra also showed that the MMA repeating units were mostly arranged in an atactic and syndiotactic configuration (Figure 6, green frame, Table 2). It is logical to assume that the spatial limitations between the graphene layers of the GIC initiator define the approach of the monomer molecules to the active centers of the propagating polymer chains, thus favoring the orientation of the MMA methyl ester groups in opposite directions.

4. Conclusions

The results obtained show that KC₂₄ can efficiently initiate the anionic copolymerization of St, MMA and EO in a one-pot fashion. The apparent yields were high, but the strongly persistent inclusion of initiator residues in the purified products (79–84%, from the amount used) obscures their reliable estimate. The copolymerization products had high molecular masses and broad dispersities, reflecting on the heterogeneous character of the copolymerization system. The chromatographic and spectroscopic analyses provided strong evidence for the segmental character of the block copolymers. While the sequence of the individual A, B and C blocks could not be firmly established, the most probable composition would be poly(ethylene oxide)-*b*-poly(methyl methacrylate)-*b*-poly(styrene)-*b*-poly(methyl methacrylate)-*b*-poly(ethylene oxide) based on the initiation mechanism and on the inability of the PEO and PMMA anions to initiate St (co)polymerization [14,19,20].

While this study offers only one example of an ABC copolymer synthesis, other combinations of π -donors (isoprene, butadiene), n - π -donors (alkyl acrylates) and n -donors (lactones, cyclosiloxanes) are certainly possible using KC₂₄ in the same one-pot approach.

Analogous to previous observations [12,26,27], the initiator was strongly delaminated (see Figure S3). Even after the filtration and extraction stages, the weight of the recovered graphite was substantially less than the initial amount used. The fact that part of the deconstructed graphenes remained firmly embedded in the polymer matrix offers new avenues for the one-pot preparation of graphene micro and nanocomposites with complex compositions and microstructures. Their characterization, mechanical properties and exploitation characteristics await future investigations.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/macromol2020012/s1>, Figure S1. Break-seal ampoule with Madagascar graphite intercalation compound KC₂₄. Synthesized–December 1989; picture taken–11 April 2022. Figure S2. Size-exclusion chromatography of cyclohexane fraction extracted after consecutive addition of comonomers St–MMA–EO and bulk copolymerization (STEM 2, Table 1). 3D plot from the M991 UVPDA Waters detector. Figure S3. Delamination of HOPG KC₂₄ during polymerization monitored by scanning electron microscopy. JEOL Super-probe 733 (JEOL Corporation, Tokyo, Japan). (a) Initial stage—graphene sheets start to separate with polymer protruding. Magnification 100 \times . (b) Final stage—sheets fully embedded in the polymer. Magnification 1100 \times . (c) Delaminated HOPG after polymer dissolution and extraction. Magnification 800 \times . HOPG—highly oriented pyrolytic graphite (Union Carbide, Houston, TX, USA).

Author Contributions: Conceptualization, I.G.; data curation, N.G.V. and I.G.; formal analysis, N.G.V.; investigation, N.G.V.; writing—original draft, I.G.; writing—review & editing, N.G.V. and I.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data obtained by this study are included in the paper.

Acknowledgments: The authors wish to thank Rashkov for the introduction to the interesting field of GIC and for many illuminating discussions. Thanks are also due to the anonymous manuscript reviewers for their critical remarks and helpful suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

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