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A Simple Approach for Preparation of High-yield Butadiene-Maleic Anhydride Copolymer Microspheres by Suppressing Diels-Alder Reaction

Hong-Yi Qi, Chen-Xi Liang, Ming-Sen Chen*, Yan-Bin Huang*, and Wan-Tai Yang*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Electronic Supplementary Information

Abstract The burgeoning ethylene production in the Asia-Pacific region has led to a substantial oversupply of butadiene as a byproduct, and it is highly important to develop new butadiene-based materials. Butadiene-maleic anhydride copolymer, characterized by its amphiphilic nature, shows potential applications in adhesives, emulsifiers, *etc*. However, the Diels-Alder (DA) reaction of butadiene and maleic anhydride competes with the polymerization, limiting the copolymer yield. In this study, the kinetics of the DA reaction and copolymerization between butadiene and maleic anhydride were examined, and the influence of various reaction conditions on the copolymer yield was investigated. We found that the DA reaction in the induction period of the radical polymerization was the critical factor in limiting copolymer yield. Therefore, we proposed the two-step method to suppress the DA reaction and achieve high-yield production (~85%) of cross-linked microspheres with controllable particle size (175–800 nm) by self-stabilized precipitation polymerization. This work enables an efficient synthesis of conjugated diolefin-maleic anhydride cross-linked microspheres, offering a novel approach to address the issue of butadiene overcapacity.

Keywords DA reaction; Radical copolymerization; Conjugated diene; Microspheres; Self-stabilized precipitation polymerization

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INTRODUCTION

Butadiene, the simplest conjugated diolefin, is mainly obtained as a byproduct of ethylene production *via* steam cracking. With the rapid increase of ethylene production in the Asia-Pacific region, global butadiene production capacity has experienced a corresponding surge.[1] In China alone, the butadiene production capacity is expected to reach 8 million metric tons/year by 2025, but only 5 million metric tons/year will be consumed mostly for conventional rubber products (*e.g.*, styrene-butadiene rubber, polybutadiene rubber, styrene-butadiene-styrene thermoplastic elastomer), which have a limited market size.[2,3] Therefore, excess butadiene would result in resource wastage, and new products based on butadiene should be developed. Among all the possible routes for butadiene-based polymers, we are particularly interested in the free-radical copolymerization of butadiene and maleic anhydride. Free radical copolymerization is a powerful method for industrial production, and maleic anhydride (MAH) is a cost-effective and environmentally friendly monomer. MAH can copolymerize with many mono-olefins (*e.g.*, ethylene, isobutylene, and styrene), and the resulting olefin-maleic anhydride copolymers can be easily converted into a series of valuable products by transforming the anhydride group into other functional groups.[4]

However, the copolymerization of MAH with conjugated diolefins is more complex than that with mono-olefins, because conjugated diolefins also undergo the Diels-Alder (DA) reaction.[5–8] The DA reaction competes for monomers with copolymerization, and the generated DA byproduct, although still possessing a C=C bond, is unable to participate in copolymerization due to the steric effect.[9] The DA reaction significantly decreased the yield of the conjugated diolefin-MAH copolymers. In 1970s, Gaylord *et al*. conducted a series of studies on the copolymerization of MAH and several conjugated diolefins (isoprene, butadiene, cyclopentadiene, *etc*.) and found the copolymer yields were lower than 60%.[10–20] They proposed that the reason limiting the copolymer yield was the DA by-reaction, but did not study how to inhibit this by-reaction and enhance the copolymerization yield. In addition to these reports in 1970s by Gaylord *et al*., there has been little research on butadiene-MAH copolymerization.

In recent years, our group has developed self-stabilized

* Corresponding authors, E-mail: dr_chen@tsinghua.edu.cn (M.S.C.)
E-mail: yanbin@tsinghua.edu.cn (Y.B.H.)
E-mail: yangwantai@tsinghua.edu.cn (W.T.Y.)

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precipitation (2SP) polymerization technology. The reaction system does not require stabilizers or dispersants, and the final products are well-defined nano- and micro-sized particles.[21] The particle products can be easily separated from the reaction media *via* filtration or centrifugation, and the solvent can be recycled and reused. These attributes of the 2SP method make it particularly relevant to industrial production. In previous studies, we utilized the 2SP method to realize the copolymerization of MAH and different monomers, including styrene,[22] acrylamide,[23] isoprene,[9] divinylbenzene,[24] and C4/C5/C9 mixed olefins.[21] Among these copolymerization monomers, isoprene is also a conjugated diene, and it was found that the yield of isoprene-MAH copolymer was lower than 30%.

In this study, we systematically investigated the effect of reaction conditions (temperature, monomer concentration, initiator concentration, and solvent) on butadiene-MAH copolymerization and DA by-reaction (Scheme 1), aiming to realize the efficient preparation of butadiene-MAH copolymer (BMAC) microspheres *via* self-stabilized precipitation polymerization. After gaining a clear understanding of the reaction system, we proposed an approach to suppress the DA by-reaction and prepared butadiene-MAH copolymer microspheres in a high yield (*ca*. 85%).

EXPERIMENTAL

Materials

Butadiene (20 wt% in toluene) was purchased from Dalian Special Gases Co., Ltd. Maleic anhydride (MAH, >98%) was purchased from Alfa Aesar. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 99%) was purchased from J&K. 1,3,5-Trimethoxybenzene (TMOB, >99%) was purchased from Sigma-Aldrich. Tetrahydrofuran (HPLC grade, >99.7%) and acetone (HPLC grade, >99.7%) were purchased from Beijing Tong Guang Fine Chemicals Company. Chloroform ($CHCl_3$, 99%) and toluene (99%) were purchased from Sino Pharm Chemical Reagent Beijing Co., Ltd. AIBN was purified by recrystallization from ethanol before use, while other reagents and solvents were used as received.

Characterization Methods

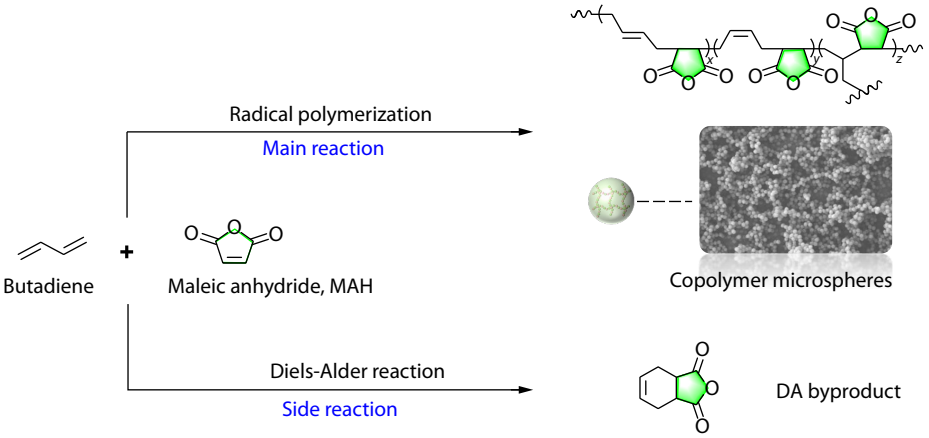
Fourier-transform infrared (FTIR) spectroscopy, ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectroscopy, elemental analysis (EA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used to investigate the reaction kinetics and confirm the chemical structures. FTIR was conducted on an INVENIO® spectrometer (Bruker) using the KBr tablet method. ^{1}H-NMR tests were conducted on a JEOL JNM-ECA600 nuclear magnetic resonance spectrometer at 298 K. The elemental contents of the copolymers were recorded on an elemental analysis instrument (Vairal EL III Elemental Analyzer). TGA tests were performed using a TG 209 F3 (NETZSCH) at a heating rate of 20 °C·min^{-1} under a nitrogen atmosphere with heating from room temperature to 800 °C. N_2 purging with a flow rate of 50 mL·min^{-1} was maintained in the sample chamber. DSC tests were conducted using a DSC-214 (NETZSCH) at a heating rate of 10 °C·min^{-1} under a nitrogen atmosphere, with heating from room temperature to 240 °C. N_2 purging at a flow rate of 50 mL·min^{-1} was maintained in the calorimeter. The morphology of the BMAC microspheres was characterized using a JSM-7401 scanning electron microscope at an electron voltage of 3 kV. The samples were sputter-coated with platinum in advance.

2SP Copolymerization of Butadiene and Maleic Anhydride

BMAC microspheres were prepared through 2SP copolymerization of butadiene and MAH. In a typical experiment, the monomer MAH (0.44 g, 4.49 mmol), the initiator AIBN (0.03 g, 2.6 wt% relative to the mass of total monomers of butadiene and MAH), and the solvent toluene (6.50 g) were added into a 25 mL round-bottom flask. After 10 min of ultrasonic treatment and 30 min of N_2 purging, butadiene (0.80 g, 14.79 mmol) in toluene (3.20 g) was added to the reaction system, which was then transferred into a thermostatic oil bath at 70 °C. Polymerization was carried out for 6 h without stirring. The product was separated by centrifugation for 5 min at 8000 r/min, then washed three times with toluene and petroleum ether, and finally dried in a vacuum oven at 80 °C to a constant weight.

Kinetic Study of the DA Reaction

The DA reaction kinetics were investigated using the ^{1}H-NMR spectroscopy. In a typical experiment, samples of the reaction solution (without the free-radical initiator) were taken at specific time points. The deuterated solvent and TMOB (as an internal standard, equal molar to the initial MAH) were added to the re-



Scheme 1 The radical copolymerization and DA by-reaction of the butadiene and MAH.

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action solution samples, which were then quenched into liquid nitrogen to terminate the reaction before ^{1}H-NMR spectroscopy analysis. The MAH conversion and DA byproduct yield were calculated by the relative area of protons using Eqs. (1) and (2), respectively.

$$\text{Conversion (MAH)}\,\% = \left(1 - \frac{3a}{2b}\right) \times 100\% \quad (1)$$

$$\text{Yield (DA byproduct)}\,\% = \frac{3g}{2b} \times 100\% \quad (2)$$

where a represents the peak area for protons adjacent to the double bonds in MAH, g represents the peak area for protons adjacent to the double bonds in 1,2,3,6-tetrahydrophthalic anhydride (the DA byproduct), and b represents the peak area for protons adjacent to the phenyl group in TMOB (Fig. S3 in the electronic supplementary information, ESI).

Kinetic Study of the Copolymerization

The copolymerization kinetic was investigated by measuring the mass of the BMAC product at specific time points. In a typical experiment, the reaction solution (0.5 mL) was extracted periodically from the system. The product was separated by centrifugation for 5 min at 8000 r/min, then washed three times with toluene and petroleum ether, respectively, and finally dried in a vacuum oven at 80 °C to a constant weight. Because the BMAC product was an alternating copolymer, the molar yield of the BMAC product was calculated from the molar of the insufficient monomer. For example, the molar yield of the BMAC product was calculated by the molar of MAH when the molar ratio of butadiene to MAH was 3.3:1 (Figs. S8–S12 in ESI).

Determination of the Gel Fraction of the BMAC Microsphere

The determination of the sol-gel fraction of the BMAC microsphere was carried out by extracting the un-crosslinked fraction in tetrahydrofuran (THF) at room temperature for 48 h. The dissolved polymer product was precipitated using excess petroleum ether. The gel and dissolved fractions were then dried in a vacuum oven at 80 °C to a constant weight. The gel fraction was calculated by weighing, using Eq. (3).

$$\text{Gel}\% = \frac{W_1}{W_0} \times 100\% \quad (3)$$

where W_0 represents the mass of the copolymer before extraction, and W_1 represents the mass of the gel fraction.

RESULTS AND DISCUSSION

DA Reaction Kinetics and Influencing Factors

To suppress the DA reaction of butadiene with MAH, we investigated the effects of reaction conditions, including temperature, reactant concentration, and solvent, on the yields of DA products over time. It should be noted that all DA products could undergo a retro-Diels-Alder (rDA) reaction upon heating above a threshold temperature, and the rDA reaction of the DA product of butadiene with MAH occurs over 147 °C.[25] The temperature of all the experiments was below 140 °C in this study; thus, the rDA reaction should not be significant in the following discussions. As the temperature increased, the DA reaction rate increased significantly (Fig. 1a and Figs. S1–S3 in ESI). When the temperature increased from 25 °C to 70 °C, the reaction time of complete conversion was reduced from 144 h to 22 h. With increasing reactant concentrations, the DA reaction also accelerated remarkably (Fig. 1b and Figs. S3–S5 in ESI). The reaction time of complete conversion for MAH initial concentration [c_0(MAH)] of 0.1, 0.5 and 1.0 mol/L was 22, 3 and 1 h, respectively. Increasing the temperature and concentration can accelerate the DA reaction. Because the DA reaction rate was moderate at a c_0(MAH) of 0.5 mol/L and temperature of 70 °C, we chose this

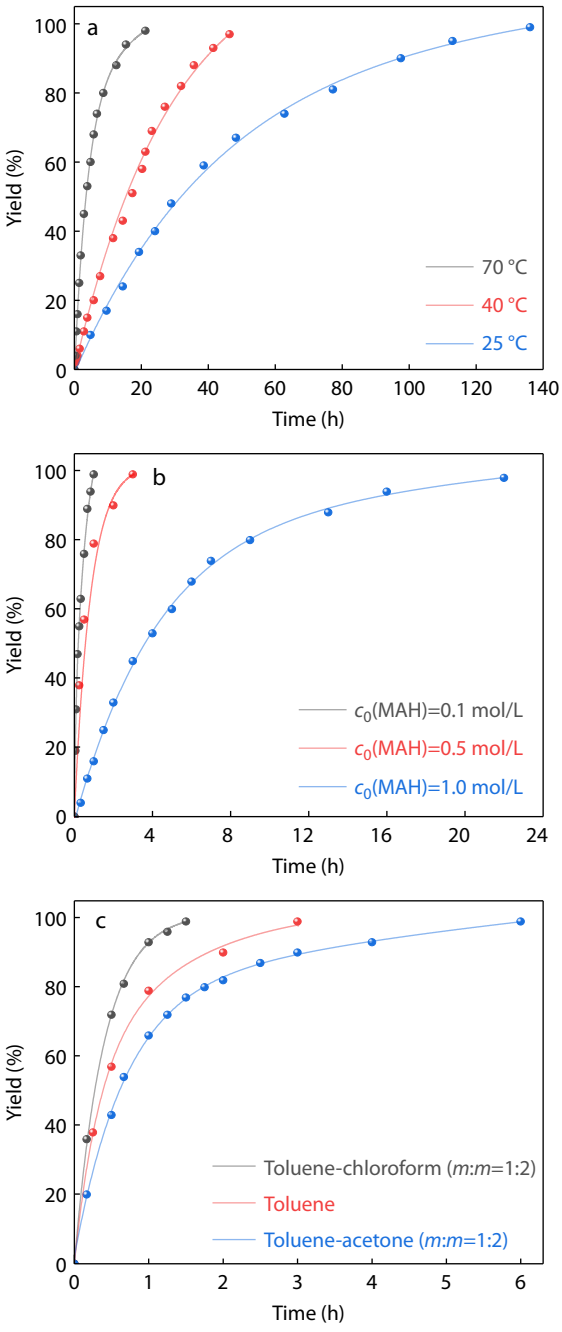

Fig. 1 DA product yields over time with different reaction conditions. (a) The effect of different temperatures on the DA reaction. Reaction conditions: c_0(MAH)=0.1 mol/L, solvent: toluene. (b) The effect of different reactant concentrations on the DA reaction. Reaction conditions: temperature=70 °C, solvent: toluene. (c) The effect of different solvents on the DA reaction. Reaction conditions: temperature=70 °C, c_0(MAH)=0.5 mol/L.

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condition to further investigate the influence of solvents.

The interactions of MAH with electron-donor solvents could influence the DA reaction,[26] so we chose three solvents (acetone, toluene, and chloroform) with different donor capacities: acetone > toluene > chloroform[27] (Fig. 1c and Figs. S3, S6 and S7 in ESI). The reaction times in the toluene-chloroform mixed solvent (toluene:chloroform=1:2 by weight), toluene, and toluene-acetone mixed solvent (toluene: acetone=1:2 by weight) were 1.5, 3, and 6 h, respectively. With a weakening of the donor capacity of the solvents, the DA reaction rate accelerated. This was attributed to the donor solvent competing with butadiene for their interaction with MAH, thereby suppressing the DA reaction.[28,29] Based on these findings, decreasing the temperature and reactant concentrations and choosing a solvent with a high donor capacity could decrease the rate of the DA reaction.

Copolymerization Kinetics and Influencing Factors

After understanding the factors influencing the DA reaction, we investigated the kinetics of both copolymerization and DA by reaction in the system with initiators (Fig. 2 and Figs. S8–S12 in

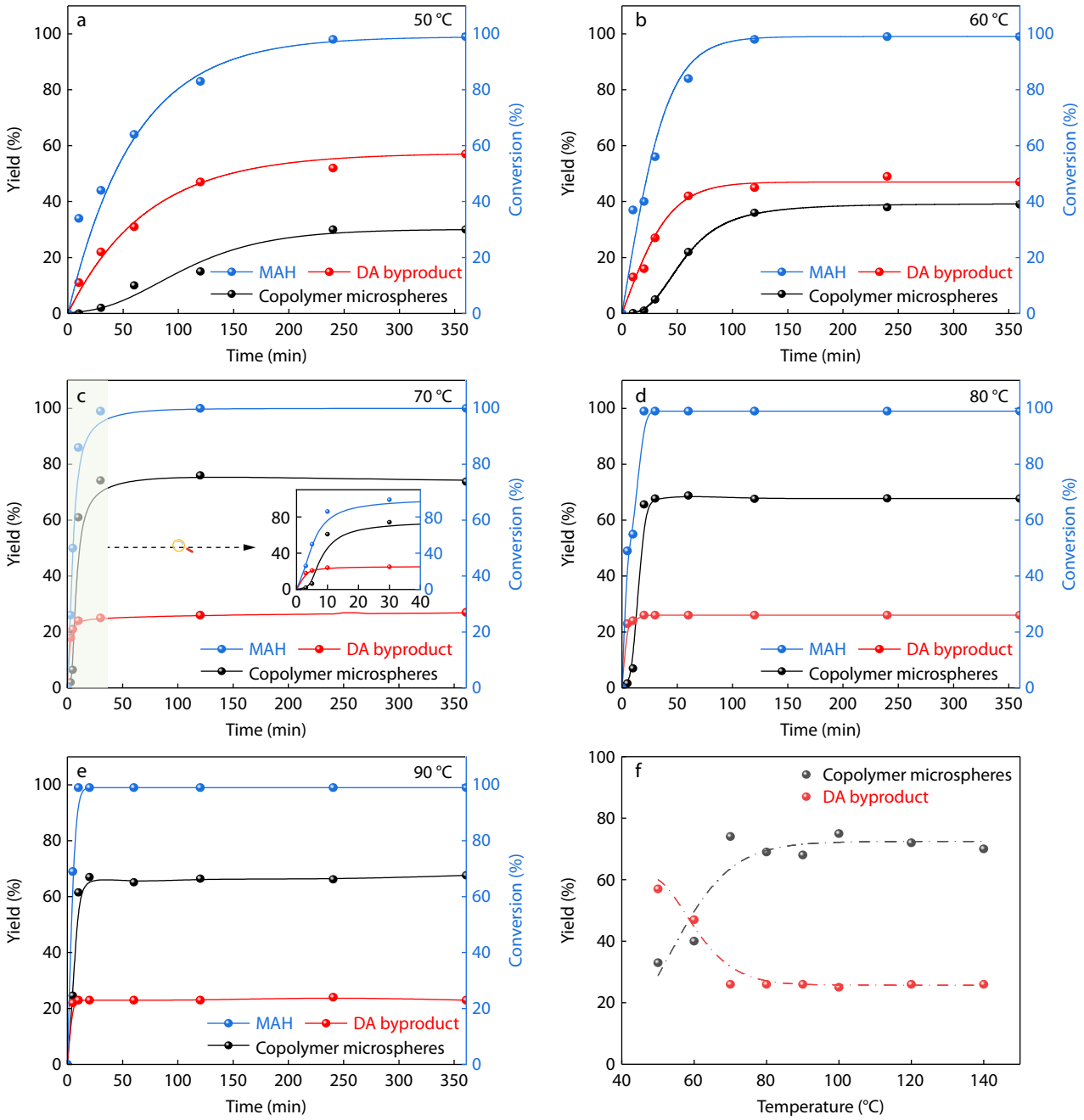

Fig. 2 (a–e) Conversions of MAH and yields of DA byproduct and copolymer microspheres over time at different temperatures; (f) Yields of copolymer microspheres and DA byproduct at different temperatures. Reaction conditions: total monomer concentration: 12 wt%, solvent: toluene, AIBN: 2.6 wt%, reaction time: 6 h.

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ESI). As shown in Figs. 2(a)–2(e), monomer MAH was consumed and converted into copolymer and DA byproducts at different temperatures. It should be noted that the copolymer product predominantly precipitated out of the reaction media in the form of microspheres, because the copolymers have very low solubility in toluene. In contrast, DA byproducts were dissolved in the solvent. As the temperature increased from 50 °C to 60 °C, both copolymerization and DA by reaction were accelerated (Figs. 2a and 2b). The DA by-reaction was always more favorable during the entire reaction, which resulted in a low copolymer yield. It should be noted that radical inhibitors or retarders would react with the initiating and propagating radicals and convert them to either non-radical species or radicals of reactivity too low to undergo propagation, resulting in the induction period.[30] Inhibitors are invariably added to commercial monomers to prevent premature thermal polymerization during storage and shipment. Many inhibitors are usually removed prior to polymerization, but small amounts of impurities (*e.g.*, oxygen) can still result in an induction period during the initial stage. For example, the induction period of AIBN in the polymerization of methyl methacrylate at 70 °C is approximately 3 min.[26] At the end of this period, when inhibitors have been consumed, polymerization proceeds at the same rate as that in the absence of inhibitors.[30] Therefore, the copolymerization kinetics showed a typical S-shaped curve. When the temperature was increased to 60 °C, the induction period of the copolymerization was shortened to 10 min, and the increase in the copolymerization rate was greater than that of the DA by the reaction rate (Fig. 2b). This contributed to a slight increase in the copolymer yield from 30% to 40%. When the temperature was further increased to 70 °C, the DA by-reaction and copolymerization were dominant at different stages, respectively (Fig. 2c). In the initial stage, the DA by-reaction was dominant. The yield of DA byproduct increased rapidly to 21% in 5 min, while the yield of copolymer microspheres was only 8%. This phenomenon should be attributed to the lack of radicals during the induction period. After the initial stage, the copolymerization reaction was dominant. The yield of copolymer microspheres increased rapidly from 8% to 70% by the time of 120 min, whereas the yield of DA byproduct increased slowly to 26%. This is attributed to the characteristics of slow initiation and fast chain propagation of free-radical polymerization. After the induction period, a large number of radicals were generated owing to the short half-life (about 4 h) of AIBN and reacted with the monomers to form chain-propagating radicals.[31,32] These chain-propagating radicals rapidly add monomers and produce copolymers at a much faster rate than the DA reaction. When the temperature was 80 and 90 °C, the reaction time was reduced to 30 min, indicating that both the copolymerization and DA by-reaction were further accelerated (Figs. 2d and 2e). However, the reaction process was similar to that at 70 °C, and yields of copolymer and DA byproducts finally increased to 70% and 26%, respectively. In fact, the yields of copolymers increased to 70% from 50 °C to 70 °C, then reached a plateau, and remained constant from 70 °C to 140 °C (Fig. 2f). This should be attributed to the DA by-reaction at the induction period. At a higher temperature, the induction period was shortened owing to faster initiator decomposition, which would reinforce the competitive nature of the copolymerization reaction and allow it to dominate at an earlier stage. However, it should be noted that the rate of the DA by-reaction also accelerated considerably at higher temperatures. In this shortened induction period, accelerated DA by-reaction had consumed part of the monomers and converted them into DA byproducts, resulting in a yield (*ca.* 26%) of DA byproduct within 5 min (Fig. 2e). Although the copolymerization reaction dominated at the subsequent stage, only a limited number of monomers could be further converted to copolymer microspheres, resulting in copolymer yield only reaching a plateau at 70%.

Moreover, the influence of initiator concentration, comonomer concentration, and donor capacity of the solvent on the copolymer yield was also investigated (Fig. 3). With initiator concentrations increasing from 0.2 wt% to 13.8 wt%, copolymer yields increased to 70% at the initiator concentration of 2.6 wt% and reached a plateau (Fig. 3a). This was attributed to the DA by-reaction occurring during the induction period. More initiators could increase the number of radicals to accelerate copolymerization and improve the copolymer yield, while the DA byproduct generated in the induction period always consumed some monomers, thus limiting the copolymer yield. When monomer concentration increased, copolymer yields remained almost constant at 70% (Fig. 3b). This was attributed to the fact that high monomer concentrations increased the effective collision probability of reactants, enhancing both the copolymerization and DA by-reaction. The effects of solvents with different donor number (DN) values on the system were also explored. The DN value represents the electron-donor capacity of the solvent. We chose a mixed solvent consisting of toluene (DN≈0.1) and acetone (DN≈17) to investigate the current system.[28] The DN values of the mixed solvents were calculated using Eq. S(1) (in ESI). As the acetone-to-toluene ratio increased, the DN values of the solvent increased gradually (Fig. S13 in ESI), whereas copolymer yield decreased slowly from 60% to 34% (Fig. 3c). This can be attributed to the complex of MAH end-chain radicals with the donor solvent. In previous studies, the complex of MAH with the donor solvent decreased the monomer concentration, suppressing both copolymerization and DA by-reaction. However, the donor solvent also forms a complex with MAH end-chain radicals to limit the rate of olefin insertion during polymerization,[4,27,28] which only weakens copolymerization. Thus, the copolymer yields decreased in mixed solvents with high DN values. Increasing the initiator concentration and choosing a solvent with low electron-donor capacity could enhance the copolymerization reaction, but the copolymer yield was still lower than 70% because of the existing DA reaction in the induction period. Therefore, we propose that suppressing DA by reaction at the initial stage is the key to improving the copolymer yield.

Based on the above findings, we focused on finding a method to efficiently suppress DA by-reaction in the initial stage. Because small amounts of radical inhibitors in the monomer and solvent would consume radicals and inhibit polymerization, the induction period is often unavoidable in the initial stage of the one-pot method. Free radicals in the initial stage were not sufficient to compete with monomers compared to DA by-reaction, resulting in a low copolymer yield. To resolve this critical problem, we chose the two-step

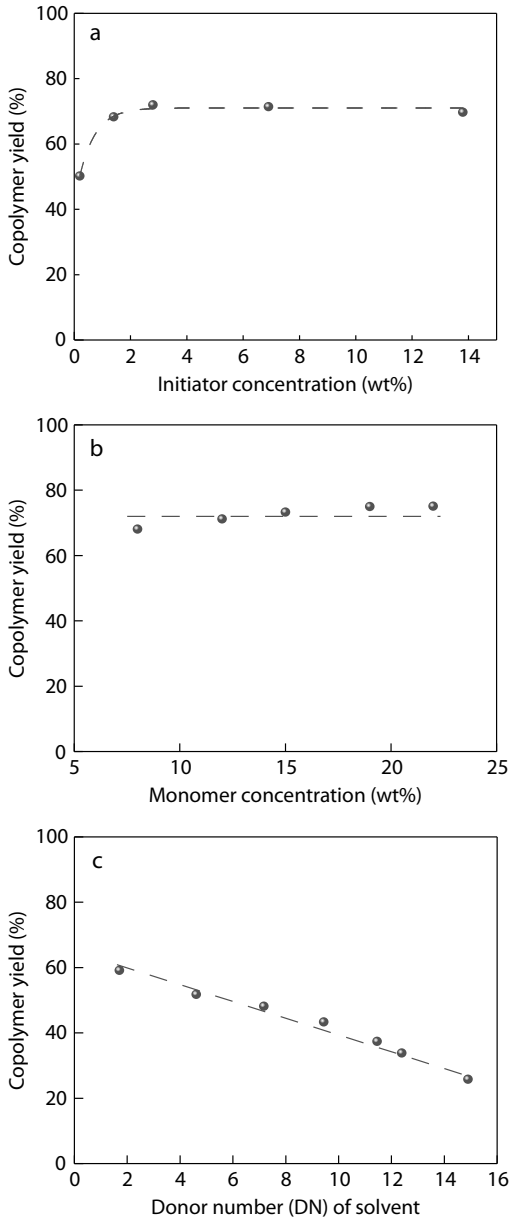

Fig. 3 (a) Copolymer yields at different initiator concentrations. Reaction conditions: temperature: 70 °C, total monomer concentration: 12 wt%, solvent: toluene, reaction time: 6 h. (b) Copolymer yields at different monomer concentrations. Reaction conditions: temperature: 70 °C, solvent: toluene, AIBN: 2.6 wt%, reaction time: 6 h. (c) Copolymer yields at different donor number (DN) values of solvent. Reaction conditions: temperature: 70 °C, solvent: toluene and acetone, AIBN: 2.6 wt%, total monomer concentration: 12 wt%, reaction time: 6 h.

method, *i.e.*, the initiator in the solvent was preheated for 30 min, and then monomers were added to the system. It should be noted that the preheating process aimed to consume radical inhibitors in the solvent, shortening the induction period during copolymerization. The experiments involving the one-pot and two-step methods were repeated thrice in parallel. The average values and standard deviations of the yields are shown in Fig. 4. As expected, the copolymer yield in the two-step method increased to 85%±2% compared to the one-pot method (70%±3%). This result confirmed our assumption and finally achieved a higher yield of butadiene-MAH copolymer microspheres.

Microspheres Morphology Evolution

After finding a method to prepare butadiene-MAH copolymer microspheres in high yield, we focused on the morphology and particle size of the copolymer products. As the temperature increased from 60 °C to 90 °C, the particle size exhibited a small increase from 580 nm to 620 nm (Fig. S14 in ESI). At higher temperatures, the number of nuclei formed in the initial stage decreased and more copolymers were deposited on the nuclei surface, leading to a larger particle size.[33] The gel fractions and particle sizes of the copolymer microspheres are summarized in Table S1 (in ESI). Owing to the difunctional properties of butadiene, the BMAC microspheres prepared in toluene were mainly cross-linked with a gel fraction over 90%. The crosslinking mechanism has been investigated and reported in our previous publication.[34] The particle size varied from 175 nm to 800 nm under different reaction conditions (Table S1, Figs. S14–S17 in ESI). We also found that the morphology of the microspheres changed from rough flower-like to smoother spherical particles with increasing temperature (Fig. S14 in ESI). This phenomenon was consistent with the results of our previous studies.[35]

For butadiene-MAH copolymerization at 90 °C, the particle size was only about 200 nm at 5 min and rapidly increased to *ca*. 420 nm at 30 min (Figs. 5a and 5b). Polymer chains first precipitated to form primary particles, and primary particles aggregated to form stable colloidal particles because of colloidal instability. Then, nascent polymers were deposited on the surface of the stable colloidal particles for growth.[33] The particle size increased slowly to *ca*. 600 nm at 120 min (Fig. 5c) and then reached a plateau. This was attributed to the decreasing concentration of the monomers and initiators. Moreover, the particle distribution at different times remained con-

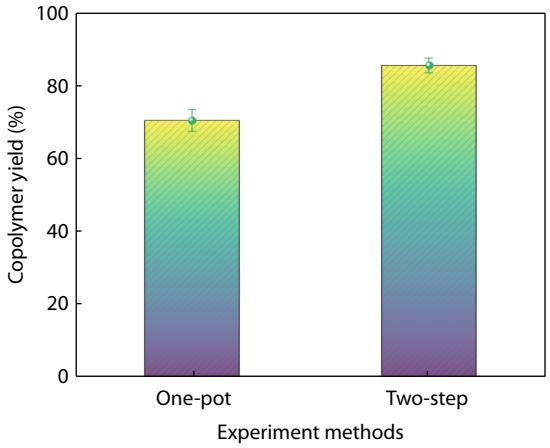

Fig. 4 Yields of butadiene-MAH copolymer microspheres with different experiment methods. The average value was recorded based on the yields of parallel experiments tested three times. For the method of two-step, the initiator in the solvent is pre-heated first for 30 min, and then monomers are added to the solution. Reaction conditions: total monomer concentration: 12 wt%, temperature: 70 °C, AIBN: 2.6 wt%, solvent: toluene, reaction time: 6 h.

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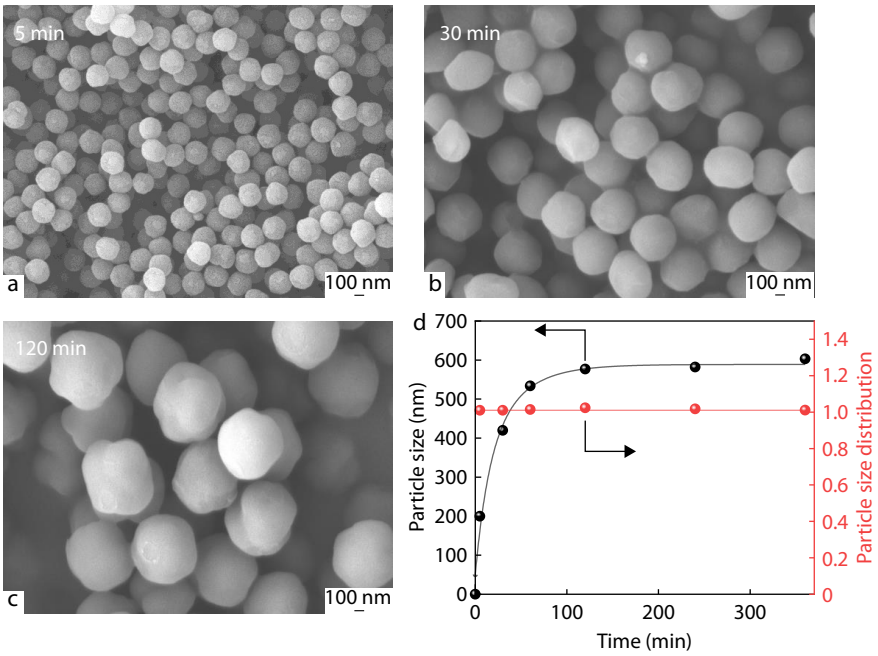

Fig. 5 (a–c) SEM images of the BMAC microspheres at 5, 30 and 120 min; (d) Particle size and its distribution at different periods. Reaction conditions: total monomer concentration: 12 wt%, temperature: 90 °C, solvent: toluene, AIBN: 2.6 wt%.

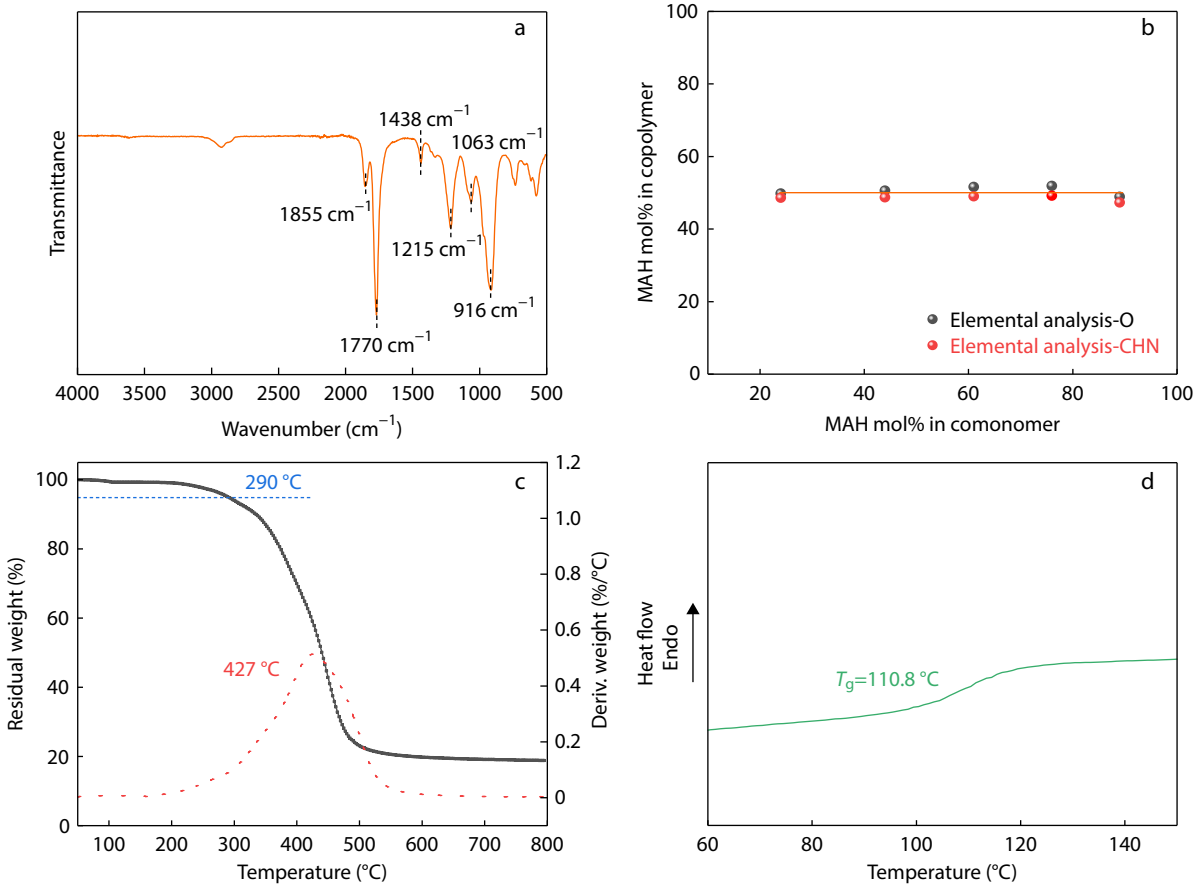

Fig. 6 (a) FTIR spectrum of the BMAC copolymer; (b) Comonomer-copolymer composition curve produced for the butadiene-MAH copolymerization; (c) TGA thermogram (20 °C/min) and (d) DSC thermogram (10 °C/min) of the BMAC copolymer.

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stant (Fig. 5d), indicating a homogeneous microsphere. In summary, butadiene and MAH were successfully converted into BMAC microspheres with controllable particle sizes *via* 2SP polymerization by altering the conditions or time.

Structure and Thermal Properties of the BMAC Copolymer

The chemical structure of the BMAC copolymer was confirmed using FTIR spectroscopy (Fig. 6a). The characteristic bands at 1770 and 1855 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of the carbonyl groups, respectively, and the bands at 1215, 1063 and 916 cm^{-1} were attributed to the C—O—C stretching vibrations.[36] These results indicated the presence of anhydride groups in the BMAC copolymer. The vibration absorption peak of the methylene $-CH_2-CH=CH-$ bonds appeared at 1438 cm^{-1},[37–39] indicating the presence of butadiene units in the BMAC copolymer. Then, we investigated the composition of the BMAC copolymers by elemental analysis. With different monomer ratios, BMAC copolymers were constantly alternating copolymers (Fig. 6b) because of the charge transfer complex of the conjugated diolefin with MAH.[9] The thermal decomposition temperature (T_{5d}, corresponding to 5% weight loss) and thermal stability of the BMAC copolymer were determined using TGA/DTG (Fig. 6c). The BMAC copolymer initially decomposed at 290 °C. The temperature corresponding to the maximum thermal decomposition rate was 427 °C, and 20 wt% of the initial mass remained after heating to 800 °C. The BMAC copolymer possessed excellent heat resistance, similar to that of commercially available styrene-maleic anhydride copolymers (T_{5d}≈300 °C).[40] As shown in Fig. 6(d), the glass transition temperature (T_g) of the BMAC copolymer was 110.8 °C.

CONCLUSIONS

In this study, the kinetics and factors of butadiene-MAH copolymerization and DA by-reaction were investigated in detail. The results revealed that the DA by-reaction in the induction period was the critical factor limiting the copolymer yields. Based on these findings, we developed a two-step method of preheating initiators in the solvent to consume the radical inhibitors, realizing the efficient synthesis of BMAC microspheres with a high yield of 85%. Microspheres with controllable particle sizes (175–800 nm) were successfully prepared *via* self-stabilized precipitation (2SP) polymerization. With our efforts, it is possible to controllably prepare various functionalized copolymer microspheres based on conjugated diolefins, offering a novel approach to address the issue of butadiene overcapacity.

Furthermore, DA byproducts can also undergo an rDA reaction when the temperature is over 147 °C, re-converting into monomers of butadiene and MAH. This nature of DA byproducts allows them to be separated from copolymer microspheres, heated at a high temperature, and re-enter the copolymerization system, thus achieving the efficient utilization of both butadiene and maleic anhydride.

Conflict of Interests

Wan-Tai Yang is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-025-3282-1.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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