Soluble Polyacrylates with Incorporating 24 wt.% Carbon Dioxide: High Transparency and Specific Ultraviolet Light Barrier Property

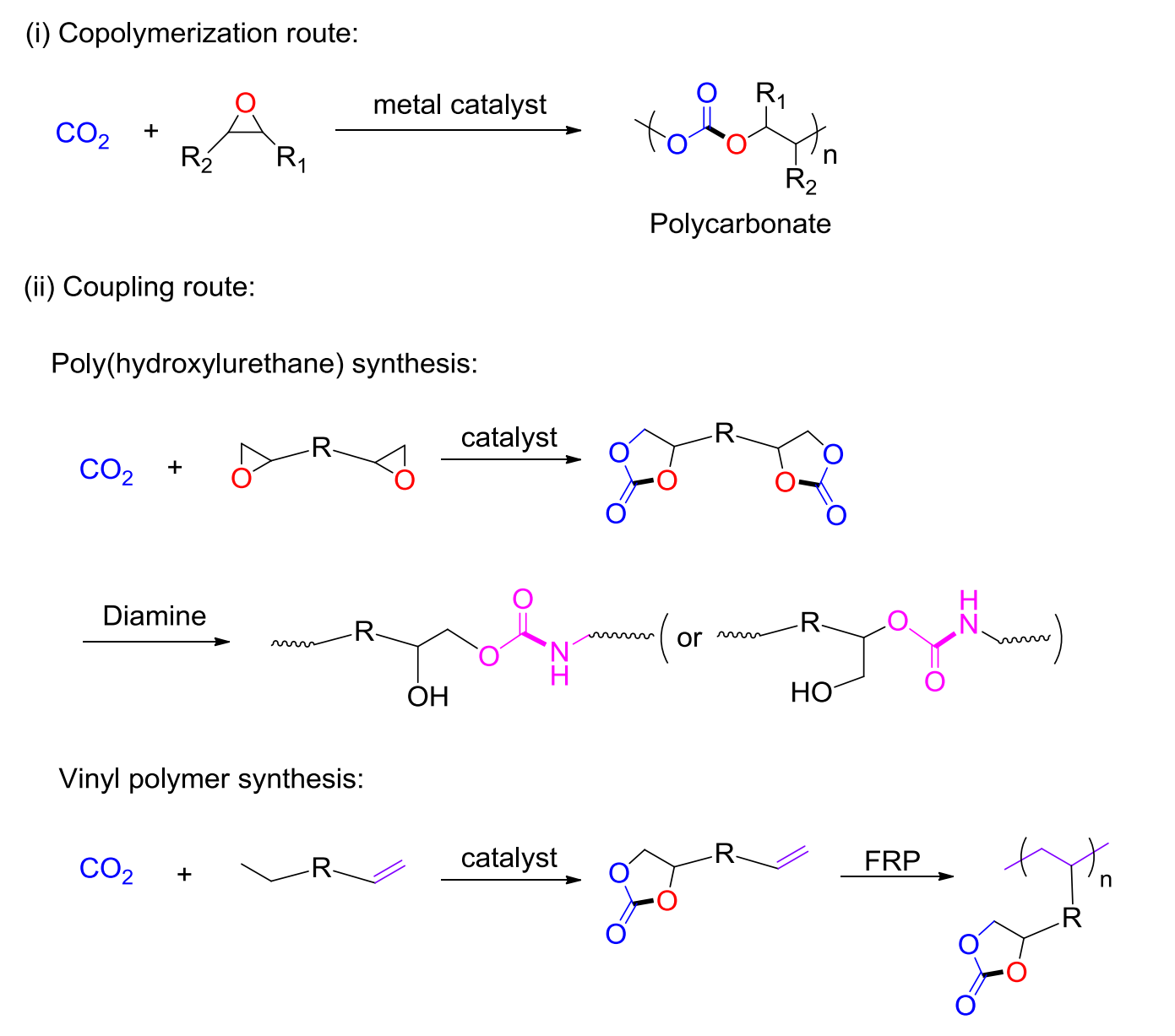
Bin Liu(21429020), Ying-Ying Zhang, Xing-Hong Zhang*, Bin-Yang Du*, Zhi-Qiang Fan
[†]MOE Key Laboratory of Macromolecular Synthesis and Functionalization
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Introduction:

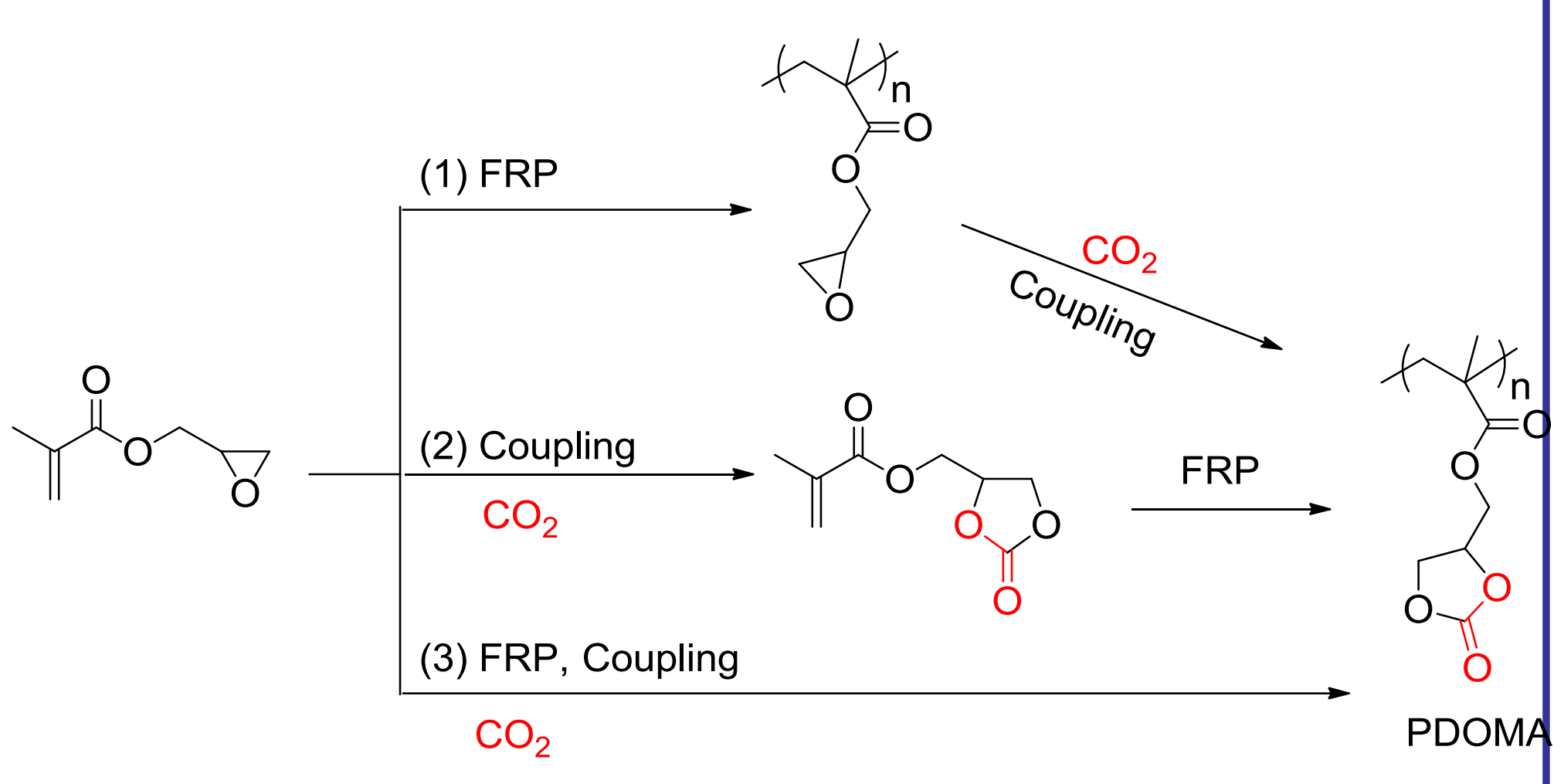
Carbon dioxide (CO_2) is an abundant, low cost, and renewable one-carbon (C1) feedstock. Transforming CO_2 into polymer is promising to achieve green and sustainable chemistry. To date, two methods are mostly used to fix CO_2 into polymers. One is the copolymerization of CO_2 with epoxides, which is a popular way to synthesize CO_2-basesd polymers (Scheme 1). The other is the synthesis of CO_2-based polymers via the cyclic carbonate intermediate derived from the coupling reaction of CO_2 and epoxides. Meanwhile, when CO_2 couples with vinyl epoxides, vinyl polymers bearing side cyclic carbonates could be synthesized via free radical polymerization (FRP). Hence, it is a practical route to utilize CO_2 by combining the coupling reaction and FRP to synthesize polyacrylates with side carbonate groups, which is valuable to investigate but rarely reported.

Experimental Section

In this work, PDOMA was for the first time synthesized from either one-pot/one-step and two-step reactions (routes 2 and 3 in Scheme 2) of CO_2 and GMA by using a binary Zn-Co(III) of DMCC/CTAB system with high efficiency. The synthesized PDOMA contained 24 wt.% CO_2 and was nearly free of metal contamination. Of importance, we described the observation on the specific UV blocking property transparent PDOMA and DOMA copolymers without aromatic structures.



Scheme 1. Copolymerization route (i) and coupling via cyclic carbonate intermediate route (ii) for synthesizing CO_2-based polymers (R_1, R_2 are substituted groups, R is a linker attached with two functional groups).



Scheme 2: Three routes for synthesizing PDOMA from CO_2 and GMA. Routes (2) and (3) are used in this work. Heterogeneous catalyst was used for the coupling reaction, FRP refers to the free radical polymerization, coupling means the coupling reaction of the oxirane group with CO_2.

1. Two-step method (routes 2)

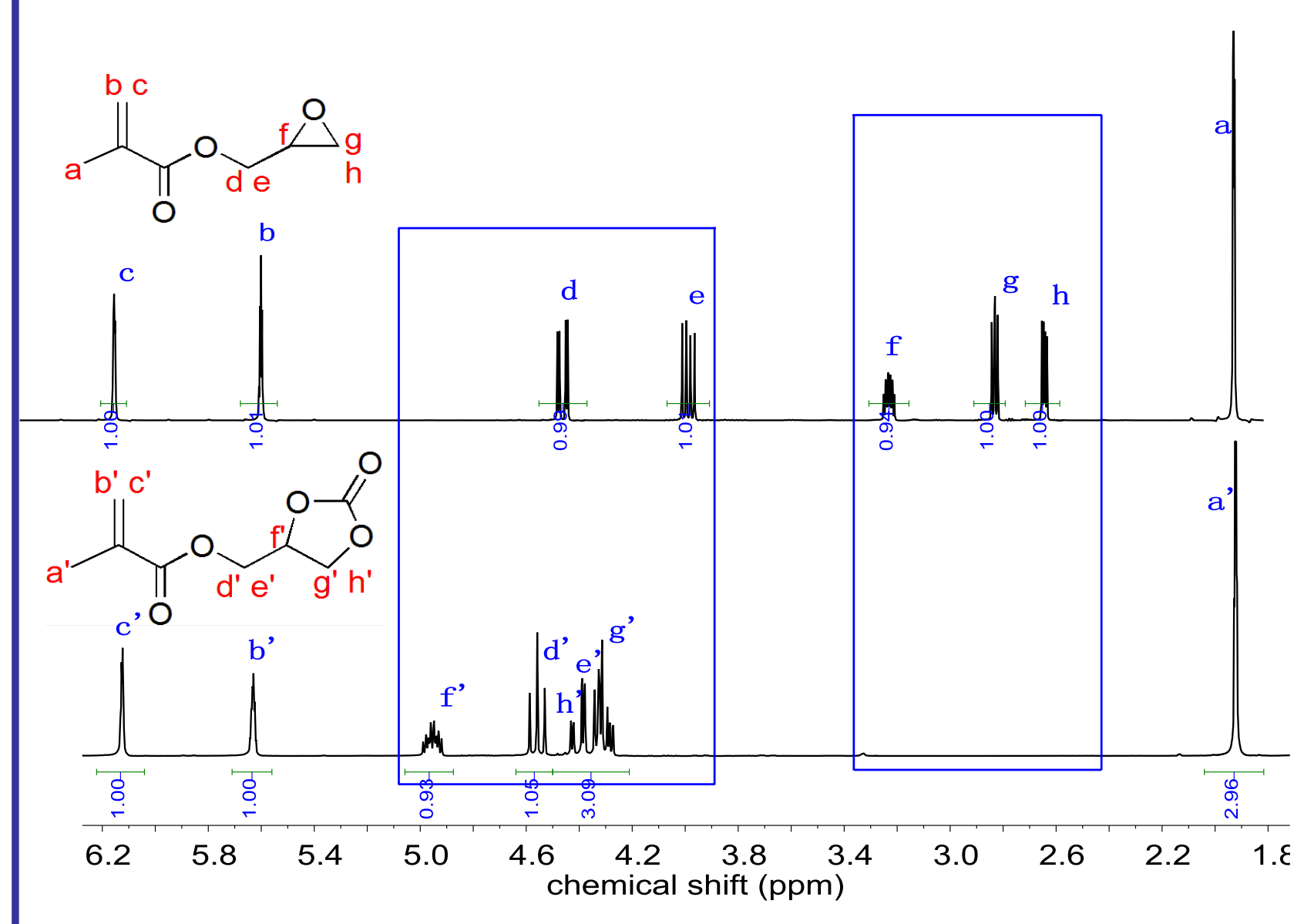


Figure 1. ^1H NMR spectra of GMA and the crude DOMA (400 MHz, $CDCl_3$).

2. One-pot/one-step method (routes 2)

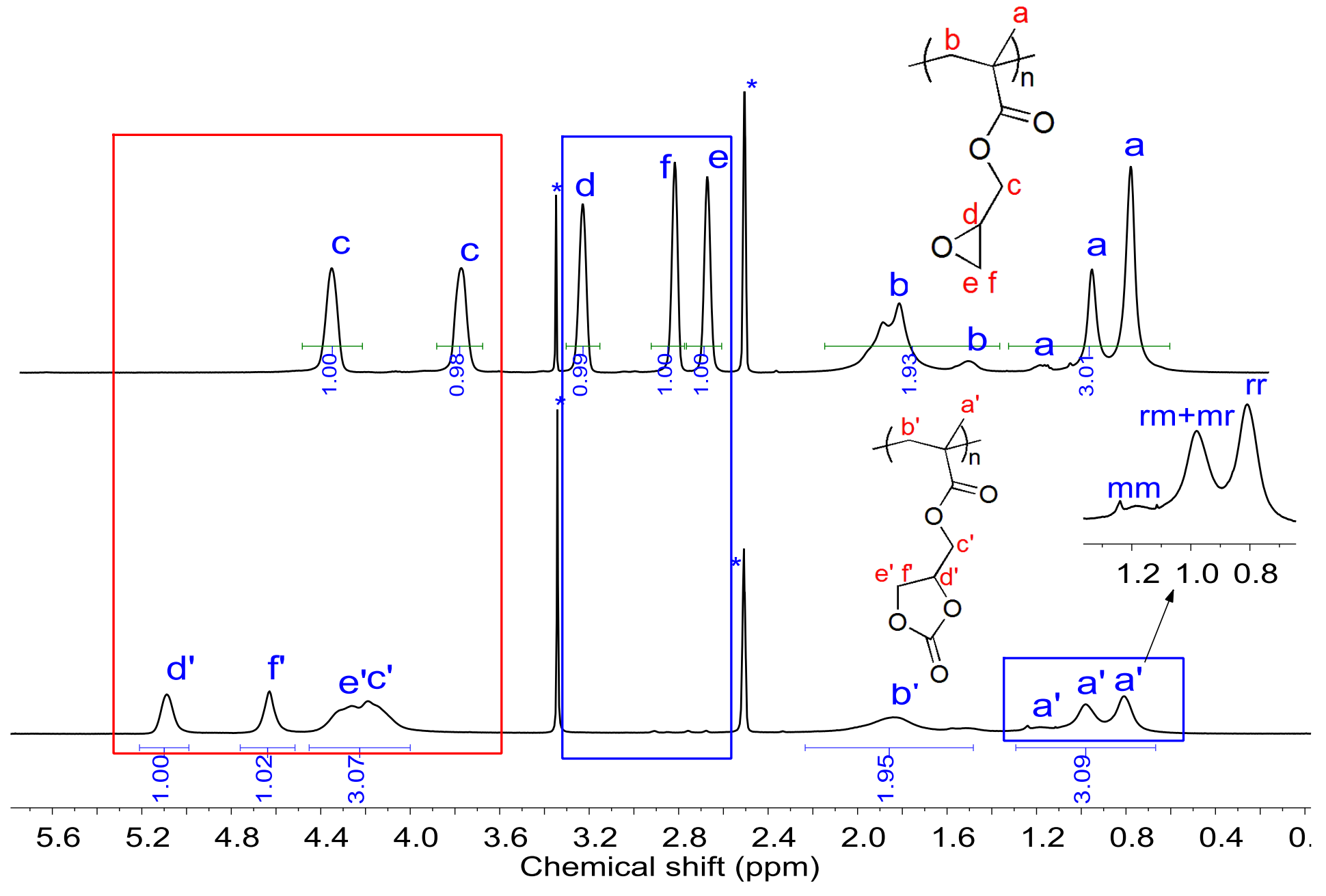


Figure 2. ^1H NMR spectra of PGMA and PDOMA (400 MHz, d_6-DMSO, Entry 8 in Table 1). (mm) and (rr) indicates the molar fraction of the isotacticity and syndiotacticity of PDOMA, which was calculated according to Lorentz fitting of ^1H NMR spectrascopy: (mm) $=A_{1.18}/(A_{1.18}+A_{0.97}+A_{0.80})$, (rr) $=A_{0.80}/(A_{1.18}+A_{0.97}+A_{0.80})$, (mr) $= 1$-(mm)-(rr).

3. Emulsion polymerization of DOMA

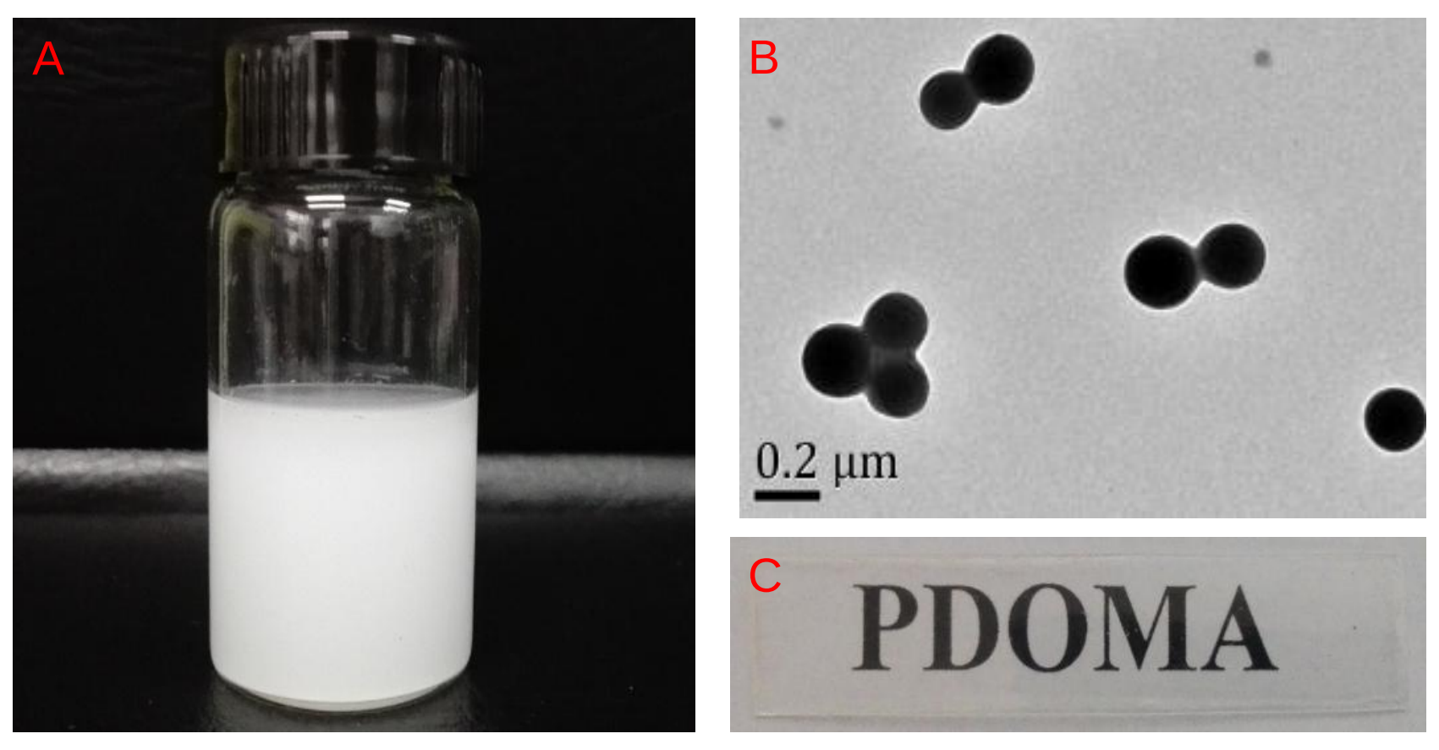


Figure 3. (A) the product after emulsion polymerization, (B) TEM images of PDOMA from emulsion polymerization , and (C) the image of the coated PDOMA with a thickness of 0.04 mm on PET film.

4. Synthesis of Poly(DOMA-*co*-MMA)

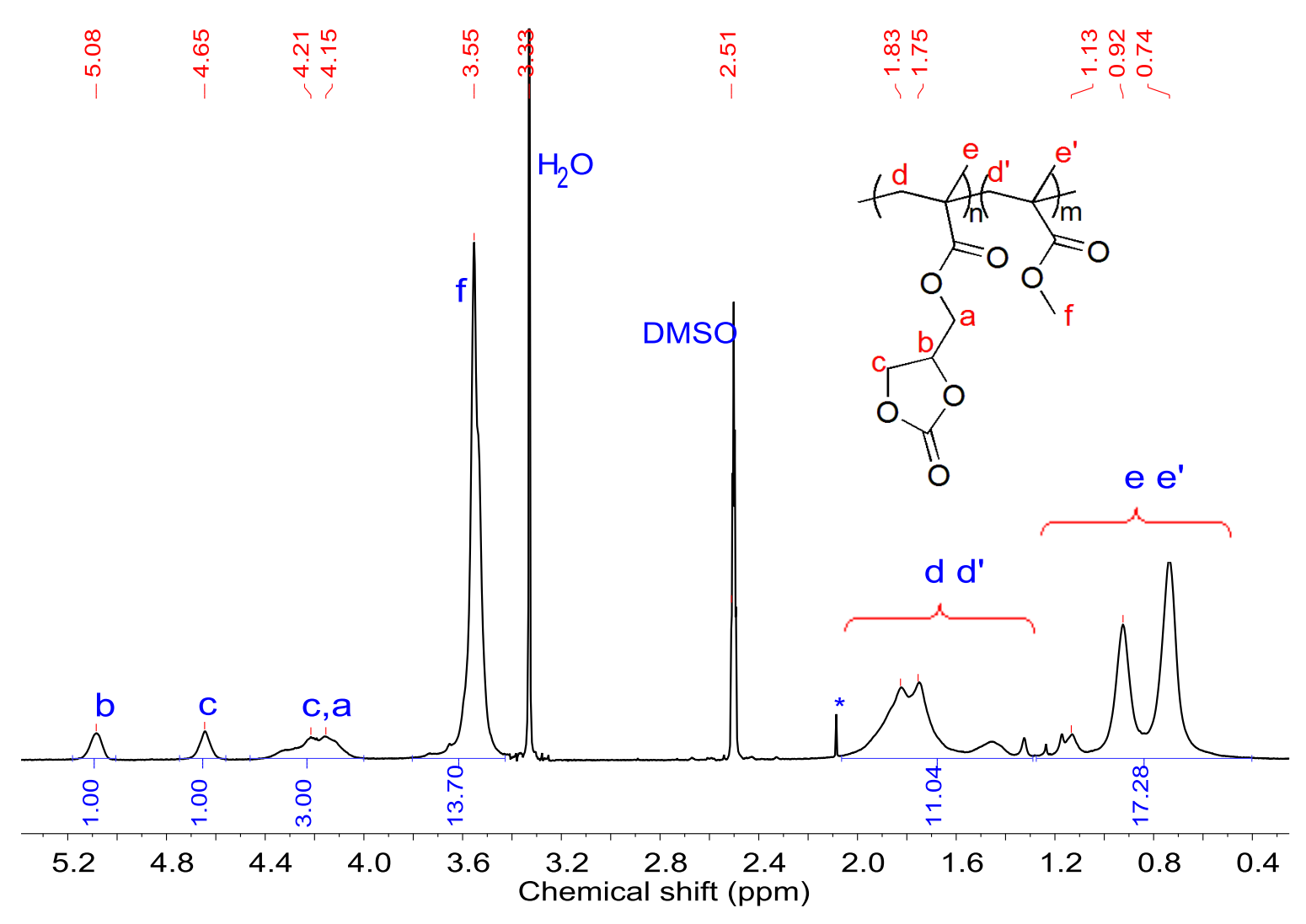


Figure 4. ^1H NMR spectrum of poly(DOMA-*co*-MMA) of entry 2 in Table 3 (400 MHz, d_6-DMSO).

Results and Discussion

1. Thermal properties of PDOMA

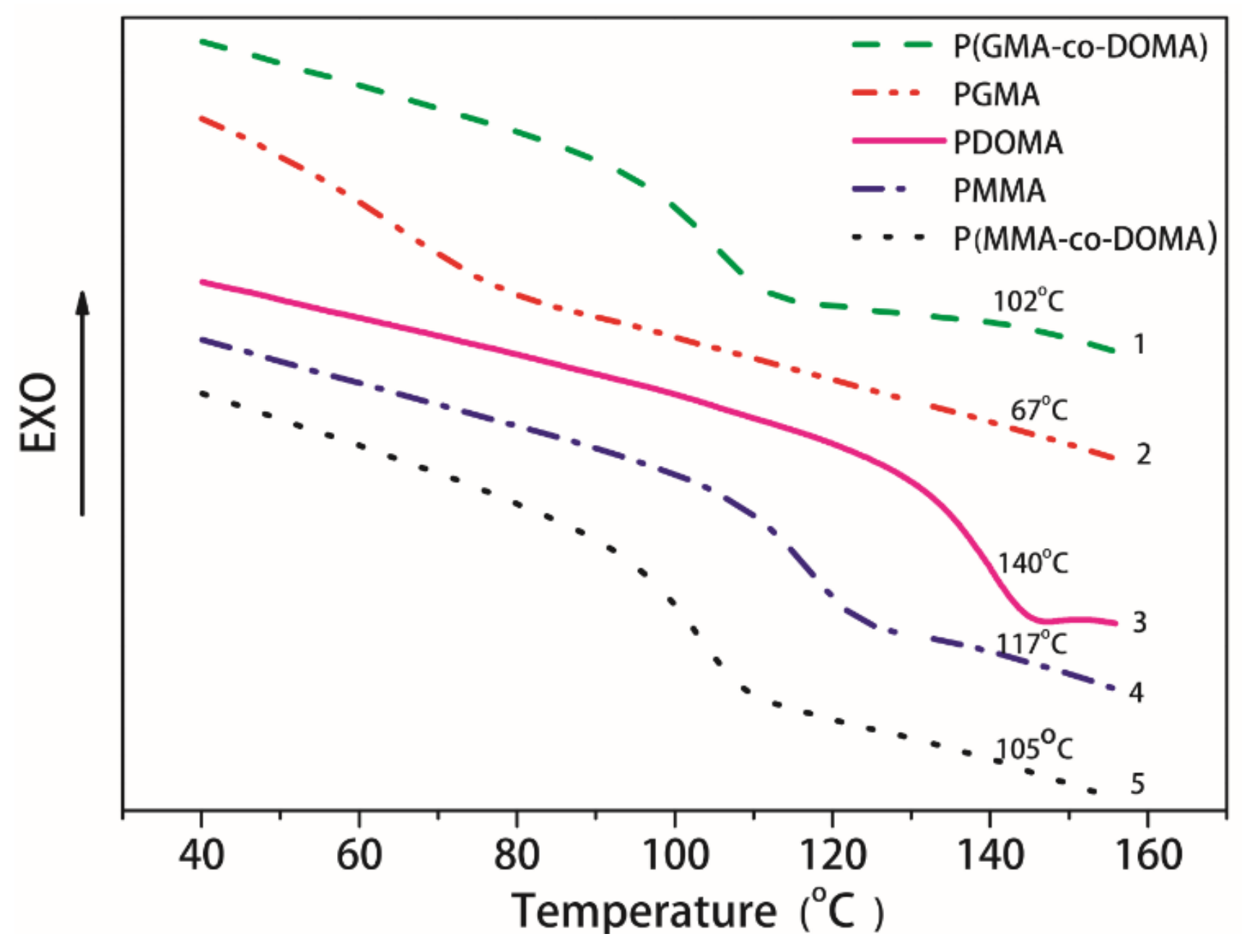


Figure 5. DSC curves of the selected polymers.

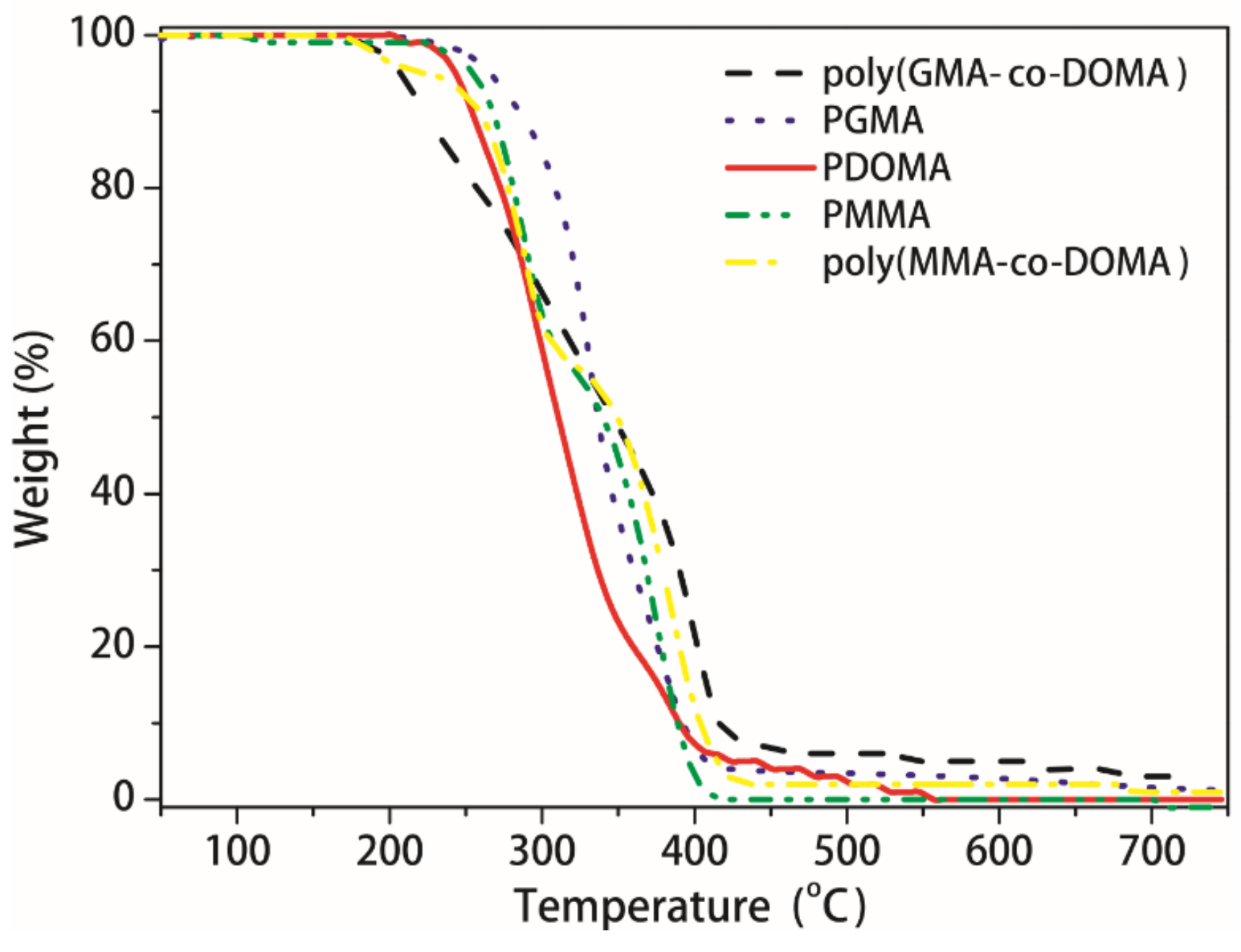


Figure 6. TGA curves of the selected polymers (the samples corresponding to the DSC samples, with a heating rate of 10 °C/min under N_2 atmosphere).

2. Optical properties of PDOMA

Table 1. Comparison of PDOMA with selected commercial polymers.[a]

Polymers	T_g (°C)	$T_{d,\ 5wt.\%}$ (°C)	Light transmittance (%)
PMMA	117	254	93%
PS	100	311	91%
PC	150	340	89%
PVC	81	170	90%
PDOMA	140	257	93%[b]

[a] These data are from ref 1; [b] Test conditions: UV-vis transmission spectrum, five PDOMA samples' average value, film thickness of 0.04 mm, 25 °C.

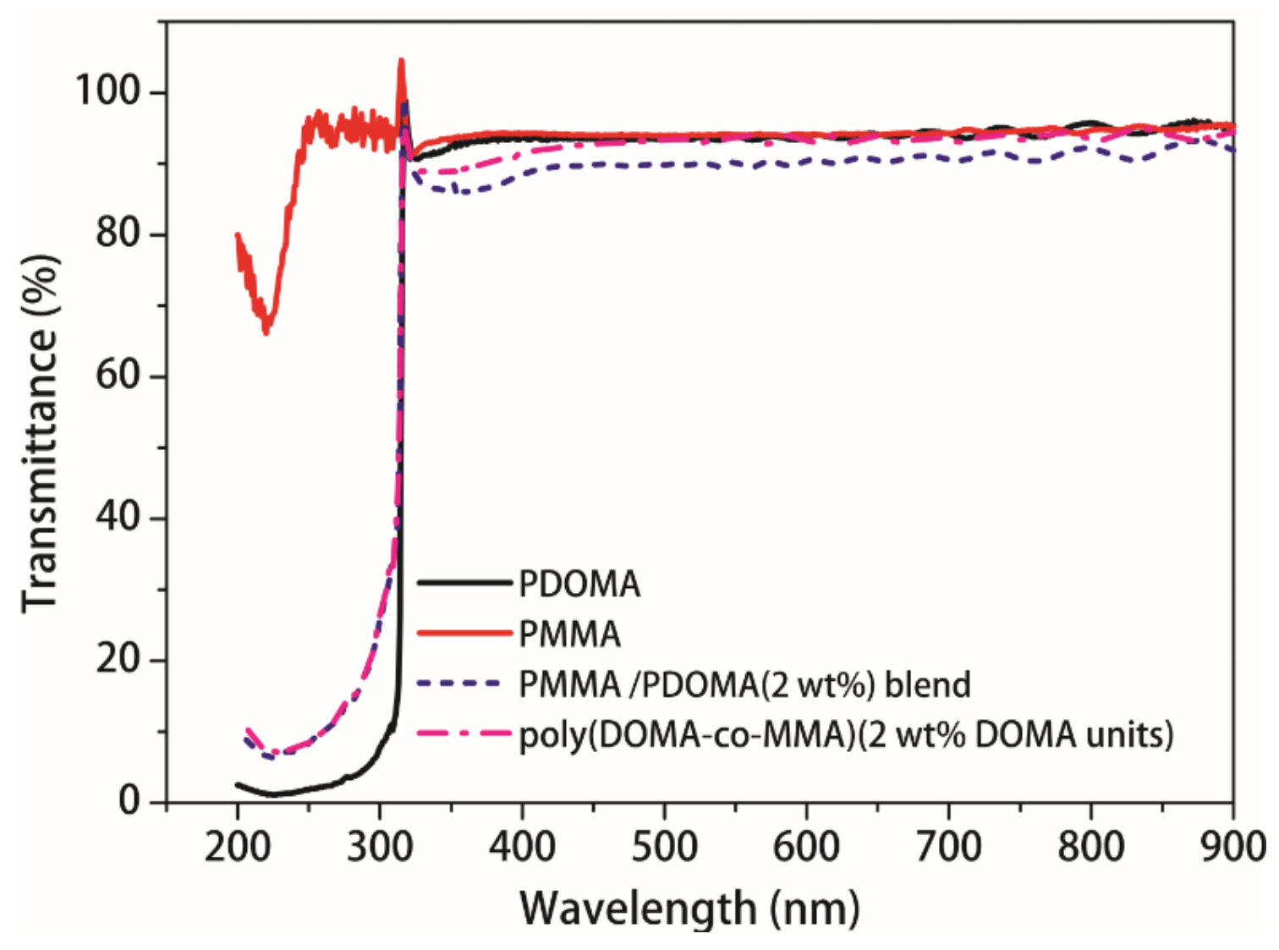


Figure 7. UV-vis transmission spectra of PDOMA, PMMA, poly(DOMA-*co*-MMA) and PDOMA/PMMA blend (thickness: 0.04 mm).

Conclusions

In conclusion, we reported the synthesis, optical and thermal properties of PDOMA with incorporating 24 wt.% CO_2 via the cyclic carbonate intermediate route. One-step reaction of GMA with CO_2 in the presence and absence of the initiators resulted in PDOMA or poly(GMA-*co*-MMA). In two-step synthesis, pure DOMA was obtained by the coupling reaction of CO_2 with GMA catalyzed by Zn-Co(III) DMCC/CTAB in a relatively large scale. DOMA could self-polymerize, and copolymerize with MMA, affording various acrylic polymers with pending cyclic carbonate moieties. The resulting PDOMAs showed tunable M_ns (12.0-132.0 kg/mol), high T_gs (121.0-140.4 °C), and high $T_{d,\ 5wt.\%}$s (257 °C). Of importance, PDOMA presented both excellent visible light transmittance and specific UV barrier property at the wavelength range of 314-800 nm and 200-313 nm, respectively. In view of application, it might be superior to the current CO_2/epoxides copolymerization route because the synthetic methods herein provided polymers without several *ppm* of metal residues. Because of strong copolymerization ability of DOMA with vinyl monomers, it will be a kind of useful vinyl monomer for modifying some common polymers via copolymerization method. Moreover, two synthetic methods we demonstrated here could be expanded to other vinyl epoxides, which will derivate many kinds of new CO_2-based polymers.

Acknowledgement

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References

1. *"Polymer Handbook"*: J. Brandrup, E. H. Immergut, Eds., John Wiley & Sons, New York, 3rd edition, **1989**.