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A novel polymerizable pigment based on surfactant-encapsulated polyoxometalates and their application in polymer coloration

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Abstract

A novel polymerizable pigment based on polymerizable surfactant-encapsulated polyoxometalate complexes has been developed. While retaining the intrinsic colors of polyoxometalates, the complexes are organically compatible and are readily incorporated into polymer matrices by means of copolymerization. During the copolymerization process, the complexes can covalently graft onto polymer chains, creating a molecular hybrid between the complexes and polymer matrices, thereby effectively avoiding phase separation between the two components which results in high transparency of the colored polymer. In addition, the complexes exhibit good coloration efficacy, provide stable colors and have little effect on polymer processibility.

Keywords: Pigment; Surfactant; Polyoxometalate; Polymer; Composite; Cluster

1. Introduction

Deliberate coloration through the use of natural or synthetic pigments is one of the oldest human activities. Due to abundant colors and high stability, inorganic pigments have been extensively used in the field of coloration [1]. However, because of the poor compatibility between inorganic components and polymer matrices, phase separation often occurs when inorganic pigments are employed as colorants of polymers, even though they are usually preprocessed into very thin powders [2]. This disadvantage induces the colored polymers to become opaque, which restricts their application in optical device fabrication. Recently, novel modification methods based on supramolecular chemistry have been developed, which provide various approaches to improve the surface properties of conventional inorganic pigments and thoroughly dispersed them throughout polymer matrices [3]. Meanwhile, the introduction of well-defined nanosized inorganic blocks such as nanoparticles and nanoclusters provides more candidates for constructing smaller and monodispersed inorganic pigments. In this background, much attention has been paid to modify the new inorganic blocks, so as to facilitate their incorporation into organic matrices and yield advanced optical materials. For example, silica coated Au and Ag particles have been doped into ureasils to form flexible hybrids with tailored colors [4].

Polyoxometalates (POMs), representing a diverse range of molecular transition metal oxide clusters with rich structures, compositions and functionalities, have been regarded as important inorganic blocks [5]. Besides their conventional properties in catalysis, redox and photochemistry, POMs readily show various colors due to the intervalence charge-transfer of mixed-valent transition metal or the incorporation of colored metal ions. In particular, the d-electron metal-substituted POMs, sometimes referred to as inorganic metalloporphyrins, can stably exhibit colors arising from the d–d transition of metal ion [6]. Stable colors, as well as the uniform nanoscale dimensions, which are advantageous to light transmission, allow POMs to have great potential in the construction of molecular pigments. However, similar to other inorganic pigments, POMs are also incompatible with polymer matrices, resulting in few reports about using POMs for polymer coloration.

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Recently, to tailor the POMs compatibility with organic systems, cationic surfactants have been applied to improve the surface properties of POM clusters [7]. The formed surfactant-encapsulated complexes (SECs) are organically compatible, while the intrinsic properties of POMs are well retained. Furthermore, we have recently successfully copolymerized a polymerizable europium-contained SEC into polymer matrices and obtained highly luminescent hybrids [8].

Following these results, we reported here for the first time the feasibility of using polymerizable SECs as molecular pigments in polymer coloration. To confirm such an approach, two cobalt-substituted POMs $K_6SiW_{11}O_{39}Co^{II}$ (Co1, pink) and $K_8Co^{II}W_{11}O_{39}Co^{II}$ (Co2, green) were selected and encapsulated by a polymerizable surfactant, dodecyl(11-methacryloyloxyundecyl)dimethylammonium bromide (DMDA), and the formed polymerizable SECs were copolymerized into polymethylmethacrylate (PMMA), a well-known optical plastic, in order to evaluate the coloration effect. The coloration efficacy, color stability and dispersion state of the SECs in PMMA matrices were all discussed in detail. Furthermore, to contrast the superiority of polymerizable SECs in overcoming the aggregation in polymer matrices, a non-polymerizable surfactant didodecyldimethylammonium bromide (DDDA) was also employed following the same procedure as DMDA.

2. Experimental

2.1. Materials

Co1 and Co2 were prepared according to the previous literature [9,10]. DMDA was synthesized following our published procedures [8], and DDDA was purchased from ACROS corporation.

2.2. The preparation of SEC

The SECs were prepared following a procedure reported previously [11]. For the DMDA/Co1 complex, Co1 was dissolved in aqueous solution, and then a chloroform solution of DMDA was added with stirring. The molar ratio of DMDA to Co1 was controlled at 5.8:1, a little lower than the exact charge ratio, in order to exhaust all the DMDA. When the pink color of the aqueous phase was completely extracted into the organic phase, the organic phase was separated and the complex was obtained by evaporating the chloroform to dryness. Other SECs were obtained in the same way.

2.3. Copolymerization of SECs into PMMA matrices

The SECs were dissolved in methylmethacrylate (MMA) with the content of 1 wt.%; slight ultrasonic energy or heat was used to speed this process. Then, 2 g of sample for each mixed solution was injected into a test tube and polymerized in the presence of AIBN (0.2 wt.%) in an oil bath at 70–72 °C. After a final 1 h standing at 110 °C to complete the polymerization, four columnar composites were obtained.

2.4. Measurements

Element analysis was performed on a Flash EA1112 from a ThermoQuest Italia S.P.A. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer 7 series thermal analysis system. FT-IR spectra were measured on a Bruker VERTEX 80V FT-IR spectrometer equipped with a DTGS detector (32 scans). Differential scanning calorimetry (DSC) measurements were measured on a Netzsch DSC 204. ^1H NMR spectra were recorded on a Bruker Ultrashield 500 MHz spectrometer. Transmission electron microscopy (TEM) images were obtained with a Hitachi H 8100 electron microscope. X-ray diffraction (XRD) was measured on Rigaku X-ray diffractometer (D/max rA, using Cu Kα radiation at a wavelength of 1.542 Å).

3. Results and discussion

3.1. Characterization of Co1, Co2 and SECs

Co1 and Co2 are Keggin-type clusters and their structural formulas can be simply described as $XCoW_{11}O_{39}$, where X is the central heteroatom (Co or Si), as is shown in Fig. 1. In Co1, only an outer tungsten atom is substituted by an octahedral coordinated cobalt atom, while for Co2, the positions of an outer tungsten atom and the central heteroatom are occupied by an octahedral coordinated and a tetrahedral coordinated cobalt atom, respectively. The different coordination types of cobalt cause Co1 and Co2 to exhibit different colors,

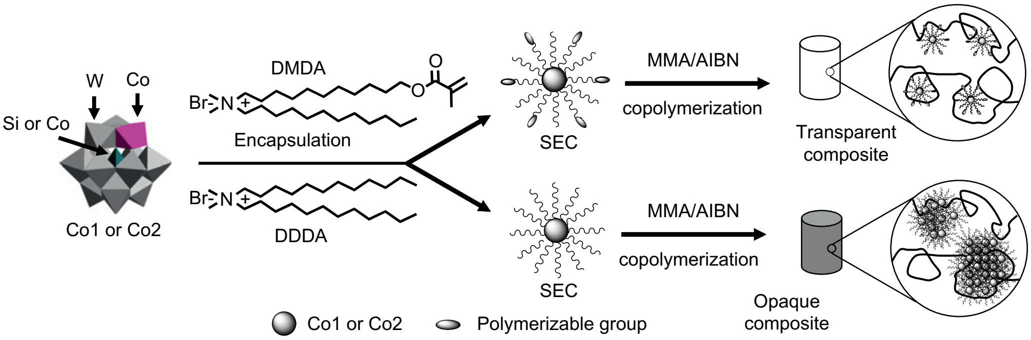

Fig. 1. The scheme of SEC preparation and their copolymerization with PMMA.

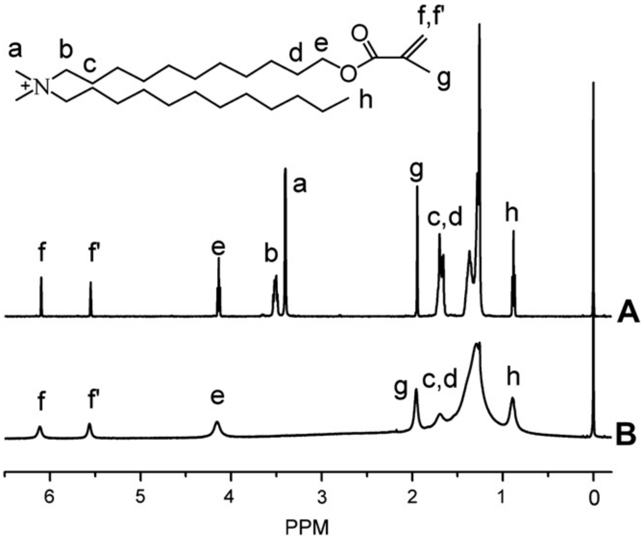

Fig. 2. ^1H NMR spectra of DMDA (A) and $(DMDA)_8Co2$ (B) in $CDCl_3$.

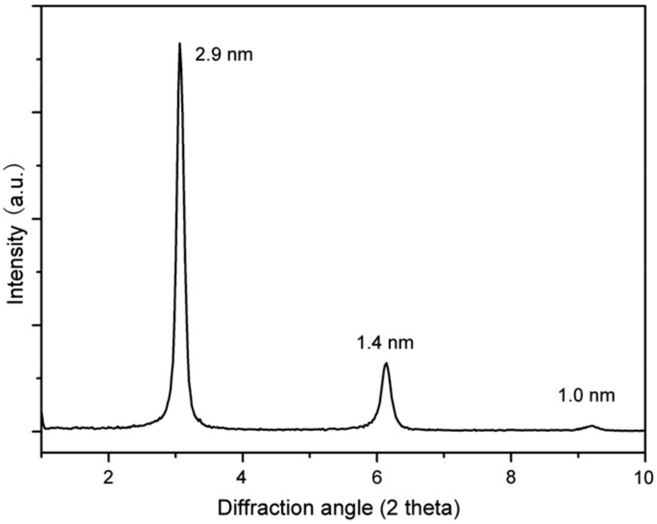

Fig. 3. X-ray diffraction of the casting film of $(DMDA)_8Co2$.

pink and green, corresponding to the broad absorption bands at around 540 nm and 620 nm (Fig. 4).

After encapsulation, the formed SECs are no longer soluble in water, but are well dissolved in organic media, such as chloroform, benzene and toluene. This implies that the hydrophilic surfaces of Co1 and Co2 have been successfully modified by the hydrophobic alkylchains of surfactants. Combining the results of elemental analysis and TGA (in Supporting information), the formulas of four SECs are $(DMDA)_6Co1$, $(DMDA)_8Co2$, $(DDDA)_6Co1$ and $(DDDA)_8Co2$, respectively, in which the total charge number of the surfactants is just equal to that of the POMs. ^1H NMR spectra also confirm the presence of surfactants in the SECs. Furthermore, in contrast to neat surfactants, the resonance signals of surfactants in SECs change greatly. For example in $(DMDA)_8Co2$, the proton signals are evidently broadened and the signals of *N*-methyl and *N*-methylene disappear (Fig. 2), as are other SECs. This is the result from the strong electrostatic interaction between surfactants and POMs, as suggested in the literature [8,11]. That is, the surfactants are immobilized on the surface of POMs, and to some extent, their mobility is confined, especially for their head regions. From the XRD results of $(DMDA)_8Co2$, we can also confirm the formation of the SEC complex. A 2.9 nm unit is observed in the layered structure, which is consistent with the total dimension of Co2 (1 nm) and surrounding DMDA shell (about 2 nm) (Fig. 3). Of significance is that the SECs exhibit characteristic infrared vibration (Supporting information) and UV–vis absorption (Fig. 4) of the POM, indicative of the well-retained structure of POM clusters and the unaltered coordination of cobalt atoms in SECs.

3.2. The compatibility between SECs and PMMA matrices

The shielding alkylchains of surfactants make SECs soluble in methylmethacrylate (MMA) in order to carry out the subsequent copolymerization. Due to the methacryloyl groups existing at the alkylchain terminal of DMDA, $(DMDA)_6Co1$ and $(DMDA)_8Co2$ are consequently polymerizable. During the

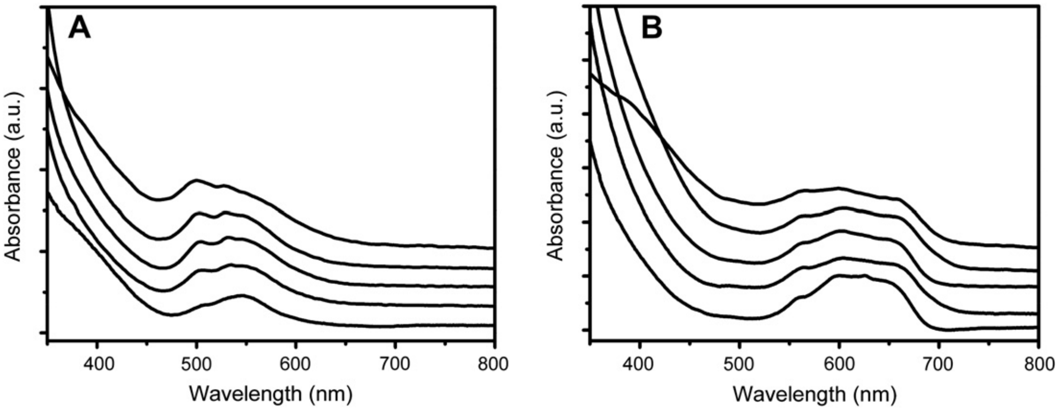

Fig. 4. (A) UV–vis absorption spectra of Co1, $(DMDA)_6Co1$, $(DDDA)_6Co1$, Co1/DMDA/PMMA, and Co1/DDDA/PMMA (from bottom to top). (B) UV–vis absorption spectra of Co2, $(DMDA)_8Co2$, $(DDDA)_8Co2$, Co2/DMDA/PMMA, and Co2/DDDA/PMMA (from bottom to top).

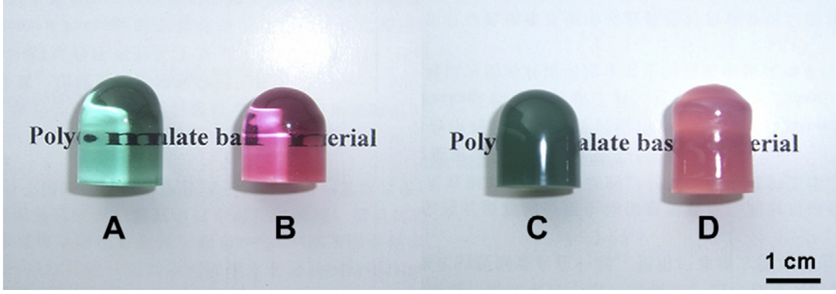

Fig. 5. Photos of the columnar composites of (A) Co2/DMDA/PMMA, (B) Co1/DMDA/PMMA, (C) Co2/DDDA/PMMA, and (D) Co1/DDDA/PMMA. Each sample contains 1 wt.% of SEC.

copolymerization process, these groups were initiated and connected with the PMMA chains. As an indication, the ν_{as}(C=C) mode of DMDA at 1638 cm^{-1} disappears completely in the SEC/PMMA composites. We have also tried to clarify the grafting position of DMDA in PMMA chains by ^{1}H NMR, but the proton signals of DMDA are fully covered by those of the PMMA components for the extremely low molar ratio of DMDA. In this instance, the SECs are well-embedded into the polymeric networks, effectively avoiding the phase separation between SECs and PMMA, and therefore the corresponding composites of Co1/DMDA/PMMA and Co2/DMDA/PMMA are transparent (Fig. 5)

However, phase separation occurs when $(DDDA)_6$Co1 and $(DDDA)_8$Co2 are used instead. Although they also dissolve well in MMA and form a transparent solution, the transparency gradually decreases with the increasing viscosity of the polymerizing solution and the final composites become opaque. This result is attributed to the aggregation of SECs in PMMA matrices. Recently, we have found that SECs tend to form spherical aggregates in organic solvents due to their amphiphilic character [12]. In the present polymerization system, such aggregation should be more intense because the small molecule solvents of MMA have grown into long chains and the solubility of SECs is reduced. The aggregation is clearly observed from the TEM images (Fig. 6); for example, in opaque Co2/DDDA/PMMA, microsized aggregates distribute everywhere, and the scales of these aggregates are larger than the wavelength of visible light. This case is actually similar to

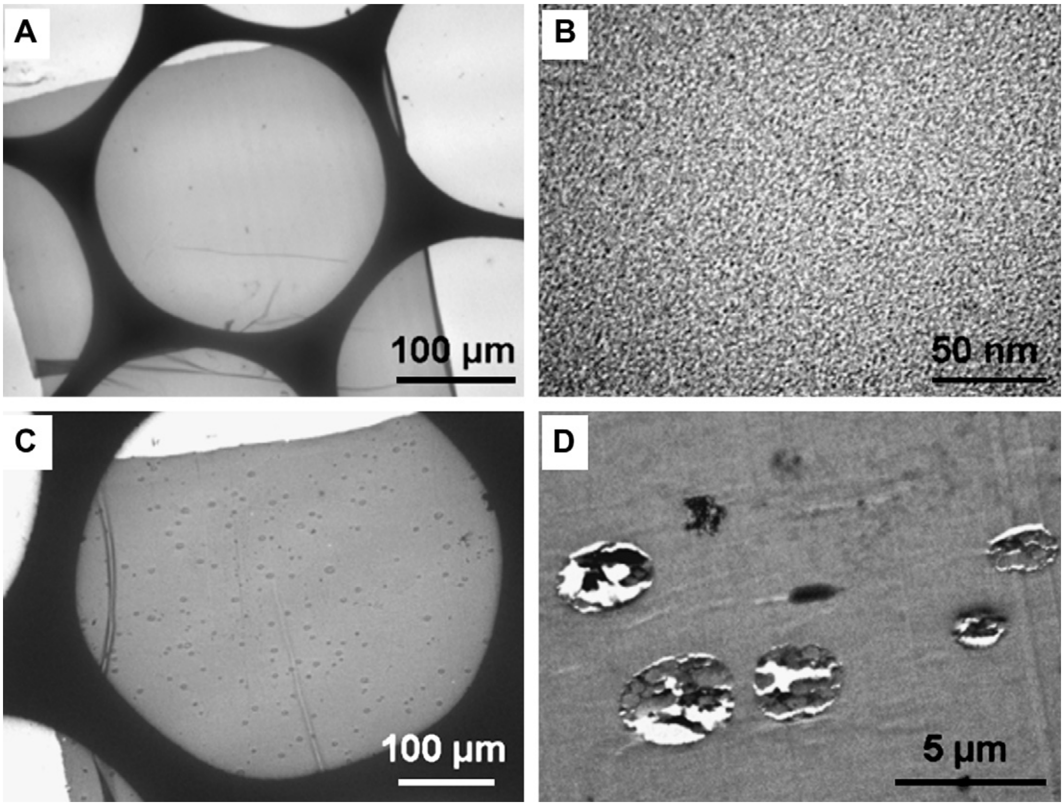

Fig. 6. TEM images of the ultrathin sections of (A) transparent Co2/DMDA/PMMA, (B) the local magnification of (A), (C) opaque Co2/DDDA/PMMA and (D) the local magnification of (C). Each sample contains 1 wt.% of SEC.

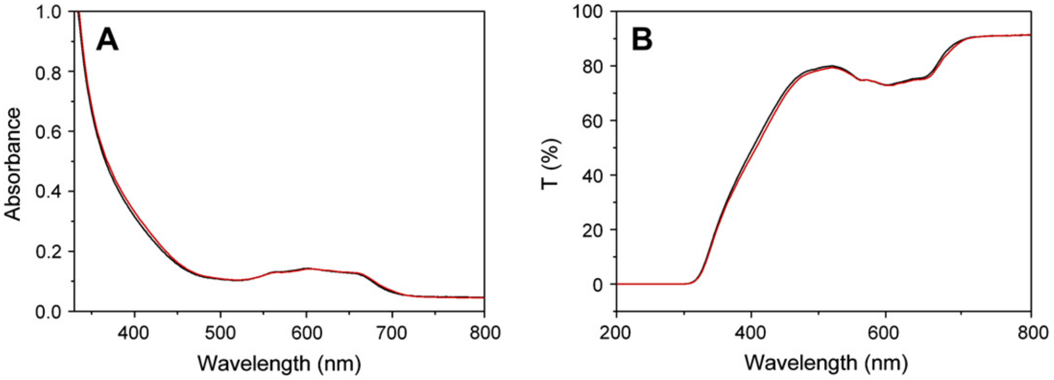

Fig. 7. (A) UV–vis absorption spectra of the 2 mm thick plates of Co2/DMDA/PMMA, freshly prepared (black line) and aged for one year (red line); (B) UV–vis transmission spectra of the 2 mm thick plates of Co2/DMDA/PMMA, freshly prepared (black line) and aged for one year (red line) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

physical blend, since there are no chemical bonds between the $(DDDA)_8Co2$ and PMMA chains. As for the transparent Co2/DMDA/PMMA composite, few aggregates, but rather nano-sized dots of SECs, are found uniformly dispersed. We presume that the initial aggregates of SECs have been broken up while the DMDA was grafting onto PMMA chains, and the formed polymeric network is essentially similar to the block copolymers (Fig. 1).

3.3. The coloration capability, color stability and other properties of SECs in PMMA matrices

In colorated PMMA, the molar content of SECs is very low because of their low weight percent of 1 wt.%, but large molecule weights around 5000. Even so, the SEC/PMMA composites still exhibit evident colors (Fig. 5), demonstrating a good coloration capability of SECs. Owing to only small portion of SECs inside, the thermal movement of PMMA chains gets little influence and the glass transitions of the SEC/PMMA composites are close to the temperature position of pure PMMA (Fig. S10 in Supporting information), which is favorable to retain the processibility of PMMA. Meanwhile, the intrinsic colors of Co1 and Co2 are also well retained in PMMA (Fig. 4), and up to now, the colors of PMMA have been stable for one year with unchanged UV–vis absorption position and intensity, as seen in Co2/DMDA/PMMA in Fig. 7. The cases for other colorated PMMA are similar which are shown in Figs. S2 and S3 in Supporting information.

The transparent composites possess excellent transmission ability to the visible light. In Fig. 8A, 2 mm thick plates of Co1/DMDA/PMMA and Co2/DMDA/PMMA exhibit transmittance higher than 90% in the range from 800 nm to the beginning of their absorption bands, which is almost the same value as that of the pure PMMA. This demonstrates that the monodispersed POM clusters have little obstruction to visible light. On the other hand, POMs generally have very intense absorption in the ultraviolet region due to the intramolecular charge-transfer from oxygen to the transition metal. The absorption intensities of Co1 and Co2 in ultraviolet bands are just hundreds of times over those of the d–d transition of their cobalt atoms in the visible band (Fig. 8B). Because the structures of POMs are well retained in PMMA matrices, the colorated PMMA also own the shielding capability of ultraviolet light. The ultraviolet light before 310 nm is fully resisted by the colorated PMMA plates, which is 60 nm broader than the pure PMMA plates. As such, these polymers are promising defencing materials of ultraviolet light.

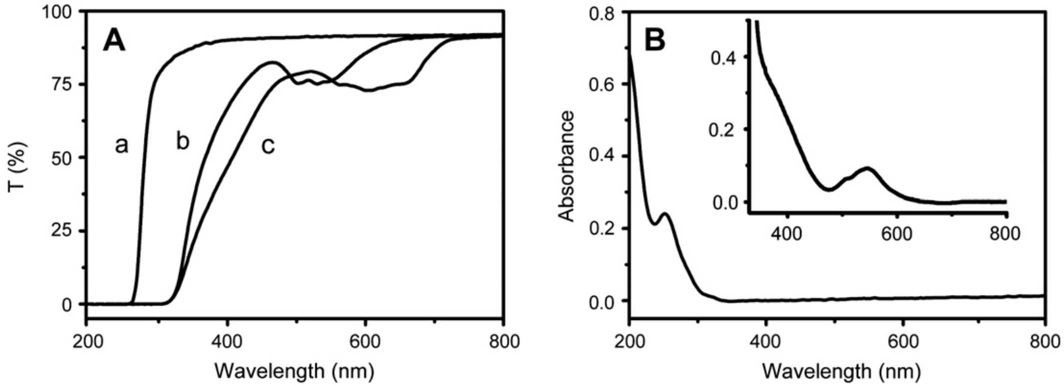

Fig. 8. (A) UV–vis transmission spectra of the 2 mm thick plates of PMMA (a), Co1/DMDA/PMMA (b) and Co2/DMDA/PMMA (c). Each sample contains 1 wt.% of SEC. (B) UV–vis absorption spectra of the aqueous solution of Co1 of 0.05 mg/ml and 5 mg/ml (inset).

Fig. 9. Photos of the columnar SEC/PMMA composites containing different colored SECs.

3.4. The applicability of SECs in polymer coloration

It should be mentioned that a significant number of free radicals are created during the polymerization process, which are oxidative to the unsaturated-valence metal atoms; therefore, the mixed-valence POMs with the colors based on intervalence charge-transfer are not adapted to the present polymerization system, such as wheel-shaped Mo_{154}. Although the deep-blue color of Mo_{154} is retained well after the encapsulation with DMDA, the blue weakens soon after the polymerization process and finally, a colorless product is obtained. Therefore, it is necessary to choose POMs containing metal ions in a stable-valence state. Following this, other metal-substituted POMs, such as $K_6SiW_{11}O_{39}M$ ($M = Mn$, Ni, Cu), are also found to be suitable for polymer coloration. Furthermore, abundant colors can be easily obtained by mixing different colored SECs and tuning their ratios in polymer matrices, as shown in Fig. 9.

4. Conclusion

In summary, a new polymerizable pigment based on surfactant-encapsulated polyoxometalate complexes has been developed. The complexes are organically compatible and the intrinsic colors of the polyoxometalate clusters are well retained. Through a copolymerization process, such complexes can be easily incorporated into PMMA matrices, achieving colored and transparent composites. The complexes show good coloration efficacy, stable colors and have few effects on the processibility of PMMA. Furthermore, because the SECs are covalently grafted onto the PMMA chains, phase separation is effectively avoided and high transparency of the final composites is thus obtained. Together with the inexpensive cost of polyoxometalate preparation and the particular optical characters of polyoxometalate, such as photochromic and non-linear optic properties, such complexes may have potential applications in the field of functional pigments for polymer coloration.

Acknowledgments

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2007.11.008.

References

[1] Noll W, Holm R, Born L. Angew Chem Int Ed Engl 1975;14:602;
Bittler K, Ostertag W. Angew Chem Int Ed Engl 1980;19:190;
Hund F. Angew Chem Int Ed Engl 1981;20:723.
[2] Bamfield P. Chromic phenomena: technological applications of colour chemistry. Cambridge: Royal Society of Chemistry; 2001;
Bilgili E, Hamey R, Scarlett B. Chem Eng Sci 2006;61:149.
[3] Sanchez C, Soler-Illia GJAA, Ribot F, Lalot T, Mayer CR, Cabuil V. Chem Mater 2001;13:3061.
[4] Boev VI, Perez-Juste J, Pastoriza-Santos I, Silva CJR, Gomes MdJM, Liz-Marzan LM. Langmuir 2004;20:10268.
[5] Pope MT, Müller A. Angew Chem Int Ed 1991;30:34;
Hill CL. Special issue on “polyoxometalate”. Chem Rev 1998;98:1;
Long D, Cronin L. Chem Eur J 2006;12:3698;
Long D, Burkholder E, Cronin L. Chem Soc Rev 2007;36:105.
[6] Pope MT. Heteropoly and isopoly oxometalates. New York: Springer-Verlag; 1983.
[7] Kurth DG, Lehmann P, Volkmer D, Cölfen H, Koop MJ, Müller A, et al. Chem Eur J 2000;6:385;
Volkmer D, Du Chesne A, Kurth DG, Schnablegger H, Lehmann P, Koop MJ, et al. J Am Chem Soc 2000;122:1995.
[8] Li H, Qi W, Li W, Sun H, Bu W, Wu L. Adv Mater 2005;17:2688.
[9] Baker LCW, McCutcheon TP. J Am Chem Soc 1956;78:4503;
Nomiya K, Kobayashi R, Miwa M. Bull Chem Soc Jpn 1983;56:2272.
[10] Tourne C, Tourne G, Malik SA, Weakley TJR. J Inorg Nucl Chem 1970;32:3875.
[11] Bu W, Fan H, Wu L, Hou X, Hu C, Zhang G, et al. Langmuir 2002;18:6398;
Bu W, Li H, Li W, Wu L, Zhai C, Wu Y. J Phys Chem B 2004;108:12776.
[12] Bu W, Li H, Sun H, Yin S, Wu L. J Am Chem Soc 2005;127:8016;
Li H, Sun H, Qi W, Xu M, Wu L. Angew Chem Int Ed 2007;46:1300.