



Proceedings of 2007 International Conference on Advanced Fibers and Polymer Materials

Oct. 15—17, 2007
Shanghai, China

Volume II

Edited by

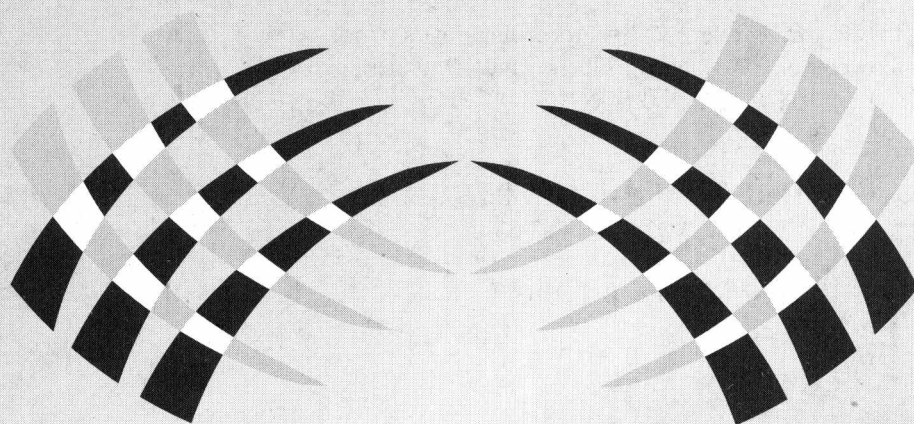
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials,
Donghua University, China

College of Polymer Science and Polymer Engineering,
The University of Akron, USA

Institute of Macromolecular Chemistry and Textile Chemistry,
Dresden University of Technology, Germany



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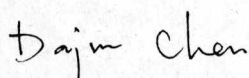
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Preface

World-wide interest in advanced fibers and polymer materials is continuing to grow rapidly. The “2007 International Conference on Advanced Fibers and Polymer Materials (ICAFPM 2007)”, under the great concerns of the worldwide scientists and scholars, is jointly organized by State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, China, Akron University, USA, as well as Dresden University of Technology, Germany. The theme of this conference is *Innovation, Collaboration and Competition*. The Conference will provide the world polymer community with an opportunity to exchange the ideas, meet old friends and make new friends as well as discuss the mission and challenges of polymer science and technology in the 21st century. To cultivate interdisciplinary activities, close interaction is needed between scientists and technologists with various areas of expertise. Hence, in addition to outstanding polymer scientists and technologists, a couple of distinguished scientists and technologists from the fields of physics, biology, chemistry, and related areas have been invited to the conference.

In the coming years, the focus of polymer research will shift more towards collaborative, interdisciplinary projects and international partnerships. Mechanisms for more efficient collaboration will be pursued as part of the mission of the conference. Other topics of general significance, such as encouraging polymer physicists, polymer chemists, materials scientists and engineers to apply their models and methods to address targeted problems in polymer fields, will also fall within the scope of the meeting. In this sense, the meeting at each turn contributes a lot to the world's polymer industry. More than 300 research articles have been accepted by this conference. It is the honor of us, the host of this conference, to gather the participants' contribution and fruits of their presentation. Therefore, we elaborately compiled the proceedings of ICAFPm 2007 and hope that the proceedings associated with the theme of this conference may coexist with the brilliant future of the world.

I hereby would like to extend our heartfelt gratitude to all the article contributors and participants of this conference, and cordial respect to all the personnel who have been making enormous efforts to ensure the success of this conference. Natural Science Foundation of China (NSFC) and some well-known companies, as well as the friendly businesspersons and schoolfellows, are also greatly appreciated for their financial support.



Dajun CHEN

General Secretary of ICAFPm 2007

Director of State Key Laboratory for Modification of Chemical Fibers and Polymer Materials

September 20, 2007

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Hyperbranched Polytriazoles Constructed by Click Polymerization

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Preparation of dendrimers and linear polymers via click chemistry is a hot topic currently due to this reaction enjoys such advantages as high yield, mild reaction conditions, and simple product isolations. Less effort has, however, been endeavored in synthesizing hyperbranched polytriazoles. We present here our recent work on constructing functional 1,5-regioregular and regiorandom hyperbranched poly(1,2,3-triazole)s from tris(4-ethynylphenyl)amine and bis(*n*-azidoalkoxy)-benzene by $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ catalyzed and thermally initiated click polymerizations, respectively. The polymers are synthesized in high yields with moderate molecular weights in short reaction time. The polymers are soluble in common organic solvents and are also processable. They possess highly thermal stability, losing merely 10% of their weights when heated to temperatures as high as 400 °C. Upon photoexcitation, all the polymers emit blue lights in dichloromethane. Whereas the emissions of 1,5-regioregular polymers shift to sky-blue in the solid state, the thin films of regiorandom one give white fluorescence due to aggregation of the polymer chains. The polymers can be readily cross-linked upon UV irradiation, generating sky-blue and white fluorescent patterns with well resolutions, respectively. The cross-linking mechanism is proposed according to the analysis by IR and UV spectroscopies.

High Performance Photopolymer and its Applications

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Abstract: A photopolymer has the potential to enhance various functions of polymers in physical, chemical and biochemical aspects. For example, (a) mechanical properties can be improved by forming a bicontinuous phase structure without decreasing optical qualities, (b) the antifouling property or heat resistance of ultra-filtration (UF) membranes can be improved by adding a photopolymerization process to the conventional wet process, and (c) the characteristics of microporous membranes can be widely controlled by preparing with photopolymerization-induced phase separation.

Key words: photopolymer; UV; phase separation; bicontinuous; microporous.

1 Introduction

Photopolymers (i.e. a polymer that is cured by light; UV polymer; UV resin) are widely used in coatings and printing ink due to their merits in curing quickly, lack of solvent needed, and providing hard coatings. Photoresist also bears a key role in the semiconductor industry.

We have been investigating different methods of providing various functions and high performances to polymer materials by using the unique characteristics of photopolymers. These include, and are not limited to, photo-patterning and quick curing capabilities, providing cross-linked polymers with *in-situ* polymerization, extensive controllability of hardness (or softness) and chemical properties, ease of copolymerization and gel formation, as well as surface modification and micro/nano phase separation abilities. Some of the topics in our investigation are introduced in this presentation.

2 Improvement of physical properties by forming a bicontinuous phase structure

Generally speaking, blends of two polymers give properties based on an arithmetical average. In a graph of property vs. composition, the properties of blends in various compositions can be plotted on a straight line which ties the property values of each original polymer. When the adhesion between the two phases is improper, the property values will fall below the line. However, it is known that the properties of blends sometimes exhibit values above the line when the blend has a bicontinuous (i.e. co-continuous) phase structure [1, 2].

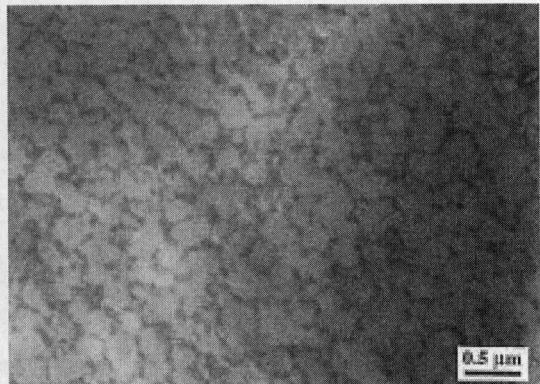


Fig. 1 A TEM image of a bicontinuous phase structure in a UV cured BPE4 / PSU (9/1 w/w) system[3]; BPE4:2,2-Bis(4-(acryloxydiethoxy)phenyl) propane; PSU:polysulfone

Polymer blends containing photopolymers form bicontinuous phase structures easily. The bicontinuous phase structure can be generated in wide range of compositions through a polymerization-induced phase separation, by photo-irradiating a homogeneous mixture of a liquid photopolymerizable monomer and a linear (thermoplastic) polymer (Fig.1) [3-5].

Curing temperature affects the degree of the phase separation and the physical properties in photopolymerization-induced phase separation. Most mechanical properties are at maximum values at the temperatures at which phase separation is incomplete, i.e. in which vague bicontinuous phases are observed with a transmitting electron microscope (TEM). It is hypothesized that bicontinuous phases are formed which have proper adhesion between the two phases. An example of tensile strength, tensile modulus, and elongation at the break for blend films are exhibited in Fig.2 [4].

Fig.3 exhibits the dependence on the composition of tensile strength and tensile modulus prepared at optimum conditions. The properties show values above the straight line which ties the values of each original polymer. It is interesting to note that the properties of blended photopolymers are enhanced even when the property values of the added linear polymer is lower than the photopolymer.

The relationship between domain size and curing temperature is shown in Fig.4 [3]. The domain sizes of the photopolymer phase are less than 0.1 μm where greater amounts of linear polymer are used. This allows films and coatings made of the blends to become transparent (Fig. 5) [3]. It is a notable character of photopolymerization that the transparent phase-separated films are realized.

3 Preparation of anti-fouling UF membrane

Ultra filtration (UF) membranes are usually prepared by wet method, in which a solution of hydrophobic linear polymer (so called "dope") is formed as hollow fibers, tubes, or as a coating onto non-woven fabric and then immersed into water to coagulate. (For example, polysulfone: PSU as a hydrophobic linear polymer and N-methylpyrrolidone: NMP as a solvent are used.)

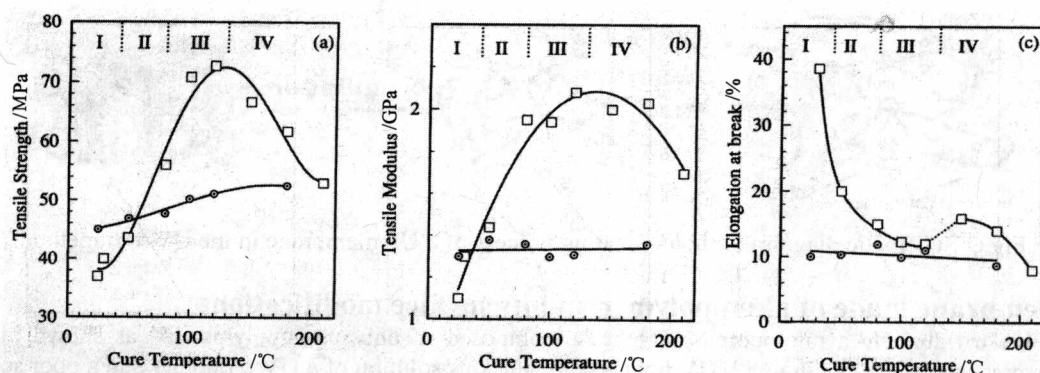


Fig.2 Tensile strength (a), tensile modulus (b), and elongation at the break (c) for blend films of photopolymerized BPE4/PSU (5/5 w/w) (□) and photopolymerized pure BPE4 (○) as a function of curing temperature [4]. Phase structure in the blends were (I) miscible semi IPN structure, (II) partially phase separated semi-PN structure, (III) vague domain structure, and (IV) bicontinuous structure.

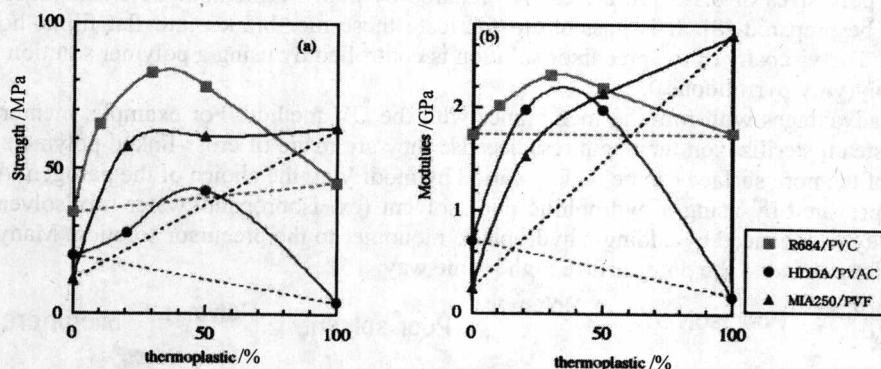


Fig.3 The dependence on the composition of tensile strength (a) and tensile modulus (b) of the blend polymers prepared at optimum conditions.

R684: Dimethyloltricyclododecane diacrylate; HDDA: Hexanediol diacrylate; PVC: Poly(vinyl chloride); PVAC: Poly(vinyl acetate); PVF: Poly(vinyl fluoride).

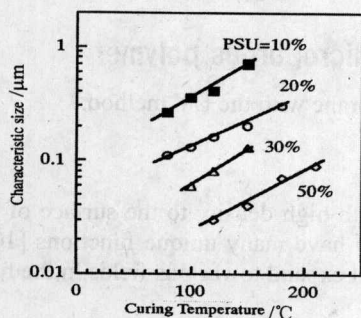


Fig.4 Relationship between BPE4-rich domain size and curing temperature for BPE4/PSU blends. [3] PSU contents are (■)10 wt%, (○)20wt% , (△)30wt%, and (◇)50 wt%.

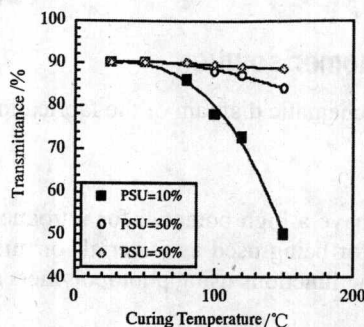


Fig. 5 Transmittance of coatings prepared by photopolymerization for BPE4/PSU system as a function of curing temperature. [3] PSU contents are (■)10 wt%, (○)30wt% and (◇)50 wt%.

In the newly developed UV-wet method (Fig.6), multi-functional hydrophilic monomer is added to the dope, which is then irradiated with UV light before the coagulation process. When the monomer-added dope is irradiated by UV, the monomer polymerizes into a cross-linked polymer in the solvent and a gel is generated. The hydrophobic linear polymer remains in solute state at this point of the process. When the gel-like dope is immersed in water, it coagulates to form an asymmetric microporous structure. The hydrophilic cross-linked photopolymer becomes entwined and fixed to the coagulated hydrophobic liner polymer in the form of a semi interpenetrating polymer network (semi-IPN), resulting in a hydrophilic pore surface [6].

In this process, the hydrophobic linear polymer is not chemically modified. Therefore, the phase diagram for coagulation is not changed. In other words, the hydrophobic linear polymer does not become water soluble. Consequently, a highly hydrophilic UF membrane can be prepared. This membrane has a high anti-fouling ability in the filtration of suspensions of sticky matter such as heavy oil and solutions of biochemical materials such as proteins. It is also possible to increase the heat-resistance of a UF membrane, by replacing the hydrophilic monomer in the above method with a monomer which gives a heat-resistant photopolymer.