Amphiphilic Silicone Copolymers for Pressure Sensitive Adhesive Applications

Sue Mecham,[1] Alan Sentman,[1] Mahesh Sambasivam[2]

[1]Polymer Solutions Incorporated, Blacksburg, Virginia 24060
[2]ConvaTec Inc., Skillman, New Jersey 08558

ABSTRACT: Amphiphilic copolymers of poly(dimethyl-siloxane)-poly(maleic anhydride-vinyl ethyl ether) (PDMS/MA/VEE) were synthesized using a polydimethylsiloxane macroinitiator. The effect of these copolymers in the properties of a silicone pressure sensitive adhesive was evaluated. The addition of the copolymers resulted in lower peel strength (more than 50% reduction) from stainless steel panel while the moisture vapor transmission rate (MVTR) showed a significant increase (8× times higher) compared to the neat pressure sensitive adhesive. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3265–3270, 2010

Key words: silicones; pressure sensitive adhesives; amphiphilic; peel strength; adhesives

INTRODUCTION

Silicone pressure sensitive adhesives are widely used in transdermal drug delivery, wound dressings, scar dressings, and other healthcare applications. These adhesives are typically a condensation product of silicate resin and polydimethylsiloxane (PDMS) fluid, or a reactive blend of vinyl- and hydride-containing PDMS cured via hydrosilylation reaction.[1] These adhesives are biocompatible and securely attach medical devices to the body when the environment is dry. However, under moist conditions such as during skin perspiration, the hydrophobic silicone adhesives lose their adhesion to skin, which can lead to the device detaching from the body prematurely. The important property that determines the performance of a pressure sensitive adhesive on skin is peel strength, which determines the force required to remove the adhesive from a surface, under dry and moist conditions. Although it is relatively easy to determine the peel strength under dry condition, the peel strength under moist conditions is rather difficult to measure. The adhesive property that determines the adhesion under moist condition is the moisture vapor transmission rate (MVTR), which determines the rate at which perspiration can diffuse through the adhesive without pooling at the adhesive-skin interface.

Traditionally, adhesion under moist environment in skin adhesives have been accomplished by adding water absorbing fillers such as hydrocolloids to pressure sensitive adhesives. The hydrocolloid fillers absorb moisture and soften, providing wet tack, thereby maintaining adhesion to skin for a longer period. However, the disadvantages of this approach are the reduction in the dry peel strength and tack properties of the adhesive due to the presence of hard fillers. In addition, because of the affinity of the fillers for water, they dissolve and leach out of the adhesive, which can leave a slimy residue on the skin after the device or dressing removal. Hence, there is a need to improve the adhesion of pressure sensitive adhesives to skin in the presence of moisture.

To improve the adhesion of silicone adhesives under a moist environment and to overcome the drawbacks of previous approaches, the present approach is to add a suitable amphiphilic silicone copolymer to a silicone pressure sensitive adhesive. An ideal amphiphilic silicone copolymer suitable for such applications should possess high cohesive strength, high MVTR, maintain adhesion even under moist conditions, and should not leach out components or leave a residue. Commercially available amphiphilic silicone copolymers are typically based on grafted poly(ethylene glycol). These copolymers are low molecular weight liquids, which are typically used as surfactants or defoamers. Addition of such low molecular weight copolymers can affect the adhesive performance because of surface migration under moist conditions and lead to a reduction in adhesion.

Correspondence to: M. Sambasivam (mahesh.sambasivam@convatec.com).

Several amphiphilic silicone copolymers have been reported in the literature. Recently, Kennedy et al.[2] published the synthesis of amphiphilic conetworks of poly(ethylene glycol) (PEG) and polydimethylsiloxane (PDMS). The amphiphilic conetworks exhibited swelling in water and hexane indicating bi-continuous phases.

Uyanik et al.[3] synthesized block copolymers of poly(vinyl pyrrolidone)-poly(dimethylsiloxane)-poly-(vinyl pyrrolidone). They prepared a di-isocyanate terminated PDMS which was then end-capped with *t*-butyl peroxide. This was used as a macroinitiator for the *N*-vinyl pyrrolidone polymerization. The resulting copolymers showed lower glass transition temperatures (T_g) than the homopolymer poly(vinyl pyrrolidone).

Graiver et al.[4] used aldehyde-functional silicones as reactive sites for vinyl copolymerization in the presence of a copper redox system. Several graft and block copolymers including polymethacrylic acid and polyacrylic acid were incorporated into the silicone polymer. These polar segments were formed by the thermal decomposition of the *t*-butyl ester substituted polyacrylate segments.

Yilgor et al.[5] synthesized triblock copolymers of polycaprolactone-PDMS, and poly(2-ethyl-2-oxazoline)-PDMS. For the caprolactone, hydroxyl-terminated PDMS was used as a macroinitiator, and for the oxazoline copolymers, benzyl chloride-terminated PDMS was used. The resulting copolymers with a silicone content of about 30–50% were shown to reduce the surface tension of plastics, such as PET, PMMA, and polyurethane.

Yildiz et al.[6] synthesized poly(*N*-isopropylacrylamide) hydrogels using diacrylate-terminated PDMS as the crosslinker. The resulting hydrogels were found to have higher compression moduli compared to the conventional crosslinker, *N,N'*-methylene bisacrylamide. This was attributed to the hydrophobic interactions between PDMS segments in the network.

This article focuses on our efforts to synthesize a novel amphiphilic silicone terpolymer and to evaluate its effect on the properties of a silicone pressure sensitive adhesive. The amphiphilic silicone terpolymer is prepared by reacting a PDMS macroinitiator with vinyl ethyl ether and maleic anhydride. The hydrophilic component of the copolymer was selected based on our preliminary work with commercially available maleic anhydride/vinyl methyl ether copolymers, sold under the tradename Gantrez. When these hydrophilic copolymers were blended into silicone pressure sensitive adhesives, the peel strength of the blended adhesives dropped under dry conditions, as expected. However, the adhesion under moist conditions improved considerably. Also, on removal of the adhesive strip from
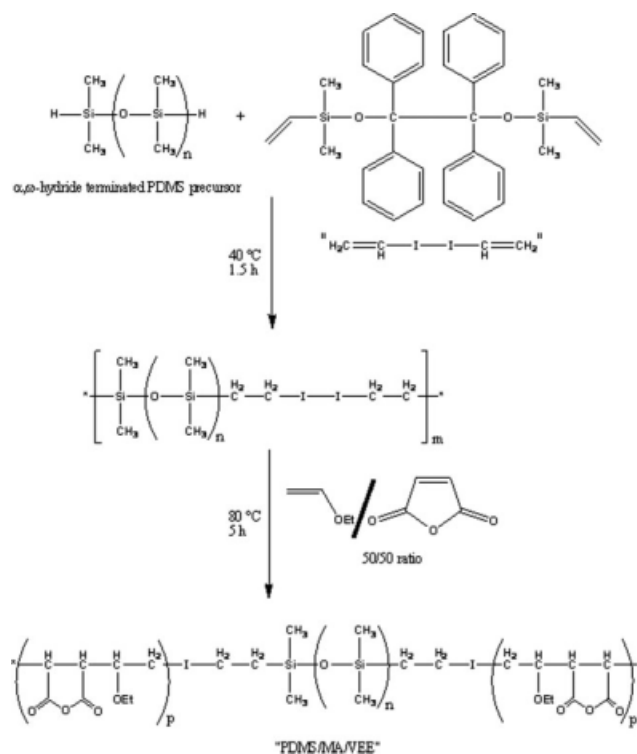
Scheme 1 Reaction scheme for preparation of amphiphilic silicone copolymers.[7]

skin under moist environment, a residue of the hydrophilic copolymer was observed on the substrate. It should be noted that Gantrez copolymers are widely used in denture adhesives for wet adhesion.

The synthesis of amphiphilic silicone copolymers is complicated due to solubility, and compatibility issues in the reaction mixture and in the polymerized state. Finding a common solvent for the monomers and the final copolymer is often challenging. We chose to use a synthetic technique published by Crivello et al.[7] which is based on a polydimethylsiloxane macroinitiator containing thermolyzable bis-(silylpinacolate) groups in the polymer backbone.

EXPERIMENTAL

Synthesis of polydimethylsiloxane-poly(maleic anhydride-alt-vinyl ethyl ether)

The synthesis of the terpolymers were based on the copolymerization of maleic anhydride and vinyl ethyl ether (PDMS/MA/VEE) using a PDMS macroinitiator (Scheme 1) according to the procedure described by Crivello et al.[7] Instead of the hydrophilic vinyl methyl ether, vinyl ethyl ether was selected due to its better oxidative stability. A reactive silicone, α,ω-hydride-terminated polydimethylsiloxane, DMS-H25, from Gelest, was used as a precursor to prepare the macroinitiator. This polymer is
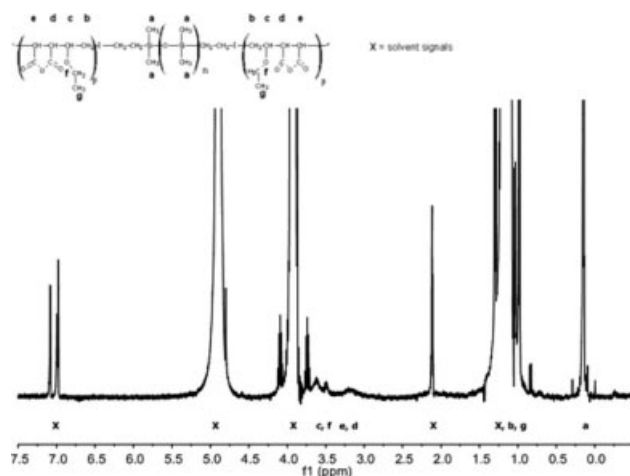
Figure 1 ^{1}H-NMR spectrum of PDMS/MA/VEE 2/1/1 terpolymer.

listed to have a molecular weight of 17,200 g/mol and about 0.01 mol % Si—H groups.

Briefly, the macroinitiator was prepared by reacting bis(dimethylvinylsilyl)benzopinacolate with α, ω-hydride-terminated PDMS precursor in the presence of Karstedt's catalyst. For the terpolymer synthesis, about 2.0 g of the polydimethylsiloxane macroinitiator was mixed with an equimolar ratio of maleic anhydride and vinyl ethyl ether in 150 mL of dried toluene in a 250 mL flask equipped with paddle stirrer, reflux condenser and nitrogen inlet. The macroinitiator to comonomer molar ratios (PDMS/MA/VEE) synthesized were 2/1/1 and 2/2/2. The polymerization was initiated by raising the temperature to 80°C and the reaction was continued for 5 h. At the end of the reaction, the terpolymer was precipitated with methanol, and dried at room temperature under vacuum. The polymerization yield was about 95% in both compositions. It should be noted that even though Scheme 1 shows a triblock structure, it is anticipated that there are diblocks and multiblocks also in the mixture.

Preparation of amphiphilic silicone pressure sensitive adhesives

The amphiphilic silicone terpolymers, PDMS/MA/VEE, were blended into a conventional silicone pressure sensitive adhesive at 20 wt % level prior to curing the adhesive. The reactive blends were then coated on a polyurethane film using a Werner-Mathis coater and cured at 150°C for 3 min. The coating thickness was about 10 mils. Peel strength of the adhesives against stainless steel was measured using an Instron at a crosshead speed of 300 mm/min. The MVTR of the adhesives was measured using 0.9% saline in an upright cup in accordance with test method ASTM E96-00.

PDMS/MA/VEE terpolymer characterization

Solubility studies

Solubility studies were carried out in deuterated methanol, 2-propanol, and toluene. In 2-propanol, and deuterated methanol, the terpolymer showed partial solubility but mainly remained as a suspension, and in toluene, it was insoluble. However, the terpolymers dissolved completely in toluene/2-propanol (1 : 1 ratio) mixture indicating the presence of both polar and non polar chain segments in the terpolymer. Even though the terpolymers were soluble in the solvent mixture, since there was no signal in GPC, the molecular weights could not be determined. The terpolymer samples when immersed in dilute alkali solution showed some swelling behavior.

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

Samples PDMS/MA/VEE 2/1/1 and PDMS/MA/VEE 2/2/2 were analyzed by ^{1}H-NMR. The terpolymers were dissolved in a mixture of in a 50 : 50 v/v mixture of nondeuterated 2-propanol and toluene-d_8 for analysis.

#### Fourier transform infrared spectroscopy

The samples were tested by Fourier transform infrared (FTIR) spectroscopy in attenuated total internal reflectance (ATR) mode.

RESULTS AND DISCUSSION

Figures 1 and 2 show the NMR spectra for the terpolymers. The two terpolymer samples produced similar signals. The large signals at 4.89 ppm, 3.92 ppm, and 1.13 ppm are due to the 2-propanol
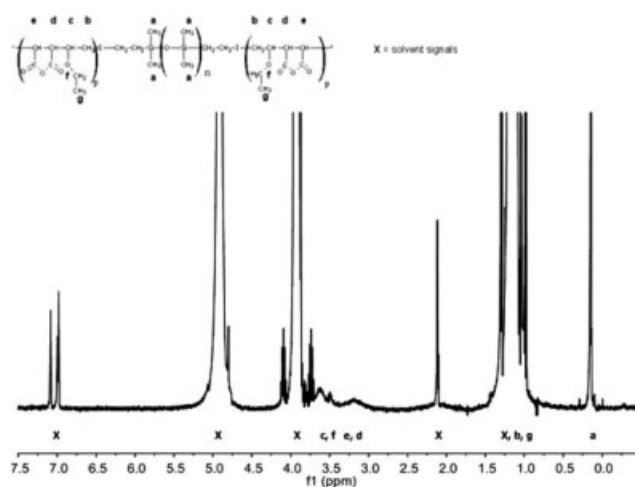
Figure 2 ^{1}H-NMR spectrum of PDMS/MA/VEE 2/2/2 terpolymer.
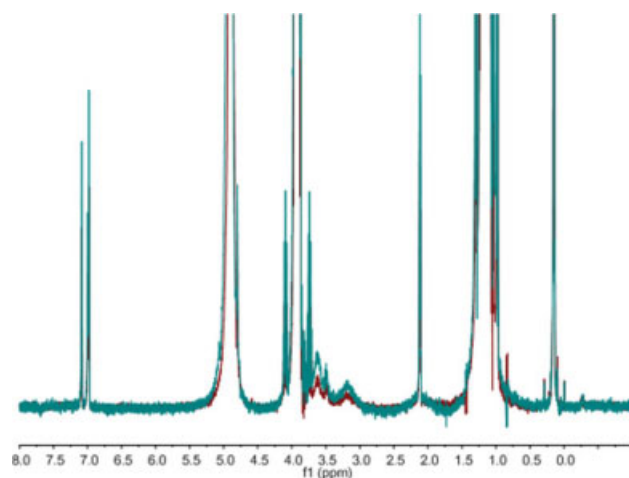
Figure 3 ^{1}H-NMR spectra of PDMS/MA/VEE 2/1/1 (maroon) PDMS/MA/VEE 2/2/2 (cyan) scaled to have matched PDMS signals at 0.14 ppm. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

TABLE I
Composition of Terpolymers as Determined by ^{1}H-NMR Spectroscopy

| Copolymer description	Weight %	
	PDMS	MA/VEE
PDMS/MA/VEE 2/1/1	63.2	36.8
PDMS/MA/VEE 2/2/2	43.5	56.5

solvent. The signals at 7.08, 6.98, and 2.12 ppm are due to the toluene-d_8 solvent. The sharp signal at 0.14 ppm is due to PDMS from the sample material. Software prediction of alternating copolymers of maleic anhydride and vinyl ethyl ether predict signals at 1.1 ppm, 1.6 ppm, and three signals between 3.3 ppm and 3.4 ppm. Any signal present at 1.1 ppm is obscured by the much larger 2-propanol signal. The signal predicted at 1.6 ppm is also not observed, and may also be obscured by the solvent if it is shifted upfield from the prediction. Signals are observed at 3.62 and 3.50 ppm which appear to correspond to the MA/VEE units. There is a broad signal around 3.2 ppm which represents a third and possibly a

fourth signal. Figure 3 shows an overlay of the two spectra, scaled to have the sample PDMS signal intensity to be equal. In this figure, it is clearly shown that the signals between 3.62 and 3.2 ppm are higher in PDMS/MA/VEE 2/2/2 than the 2/1/1 terpolymer which matches expectations based on the stated terpolymer ratios. If it is assumed that the MA/VEE in these samples is an alternating copolymer of maleic anhydride and vinyl ethyl ether, the three signals at 3.62, 3.50, and 3.2 ppm are consistent with five protons from the copolymer, and the ratio of MA/VEE to PDMS can be calculated. The results of these calculations are shown in Table I.

Figure 4 shows the FTIR spectra for the PDMS/ MA/VEE terpolymers overlaid with the PDMS precursor (bottom curve). The precursor shows fingerprint bands at 1258 cm^{-1} (Si—CH3), 1067 cm^{-1} and 1013 cm^{-1} (Si—O—Si stretching vibration), and 793 cm^{-1} (Si—C stretching and CH$_3$ rocking) for PDMS. The terpolymers show distinct bands at 1856 cm^{-1} and 1781 cm^{-1} which can be attributed to anhydride group. A reference spectrum of maleic anhydride/ vinyl methyl ether (Gantrez^{TM} AN-169) provided in Figure 5 provides a close match to the terpolymer samples in Figure 4, which confirms the presence of PDMS and MA/VEE moieties in the copolymers.
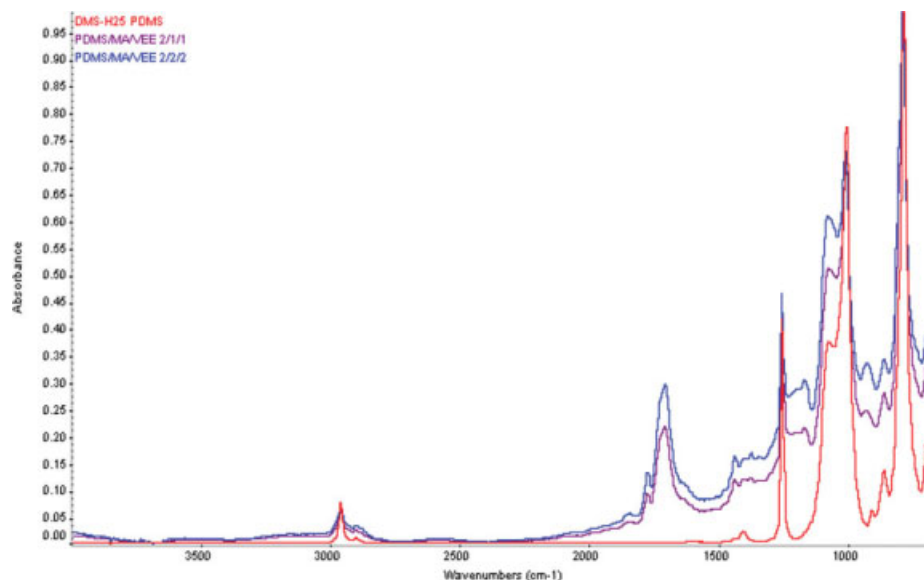
Figure 4 FTIR of PDMS/MA/VEE terpolymers and PDMS starting material. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
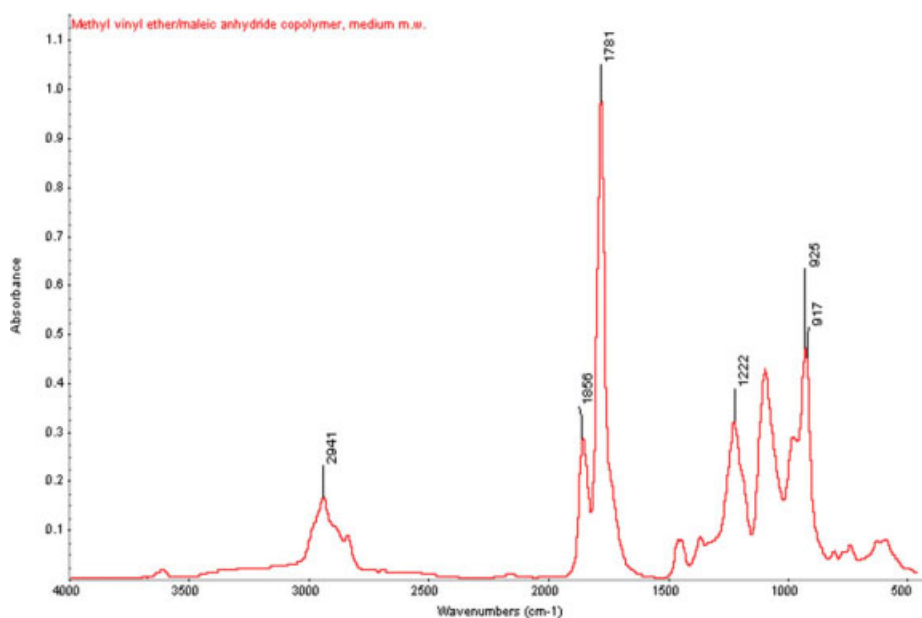
Figure 5 Reference FTIR of MA/VME Copolymer (Gantrez^{TM} AN-169). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Amphiphilic silicone PSA properties: peel strength and moisture vapor transmission rate

Figure 6 shows the results of the peel strength, and moisture vapor transmission rate tests. It can be readily seen that blending the high T_g amphiphilic terpolymers into the adhesive, lowered the peel strength of the adhesive considerably. However, the moisture vapor transmission improved significantly by the addition of the terpolymers. The MVTR results do not vary much between the two terpolymer compositions since the majority of the component in the adhesive is silicone. It should be noted that there was no component leaching out of the adhesive when the compositions were tested under moist conditions, indicating that the terpolymer was not solubilized in moisture.

SUMMARY

Amphiphilic silicone terpolymers were synthesized based on a polydimethylsiloxane macroinitiator containing thermolyzable bis(silylpinacolate) groups in the polymer backbone. The terpolymers show solubility in a toluene/2-propanol mixture but not the individual solvents indicating the presence of covalently bonded hydrophobic and hydrophilic segments. The presence of both PDMS and MA/VEE components are confirmed by the NMR, and FTIR. A microphase separated block structure is indicated by the solubility characteristics of the terpolymers. Blending these amphiphilic terpolymers into silicone pressure sensitive adhesives resulted in an increase

in the MVTR, however, the peel strength reduced significantly.

We believe that this is the first time the use of an amphiphilic silicone terpolymer in a silicone pressure sensitive adhesive is reported with a demonstrated increase in the MVTR of the adhesive. Although one could achieve a similar increase in MVTR by blending in hydrophilic polymers, the current approach is superior because the amphiphilic copolymer will not leach out of the adhesive in the presence of moisture. In addition, the selection of a hydrolysable monomer such as maleic anhydride, is expected to improve the adhesion to skin under moist conditions. This will be studied further.
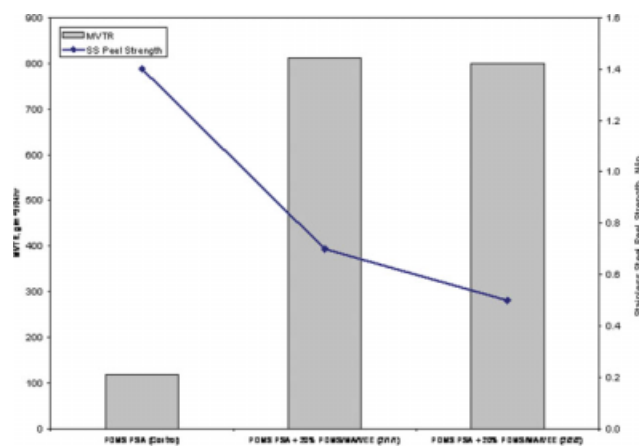
Figure 6 Effect of PDMS/MA/VEE terpolymer on the MVTR and peel strength of silicone PSA. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

References

1. Thomas, X. Silicone Adhesives in Healthcare Applications, Dow Corning Literature; Dow Corning Corporation: Midland, Michigan, 2003.
2. Edrodi, G.; Kennedy, J. P. J Polym Sci Part A: Polym Chem 2005, 43, 4954.
3. Uyanik, N; Koker, B; Yildiz, Y. J Appl Polym Sci 1999, 71, 1915.
4. Graiver, D.; Decker, G. T.; Kim, Y.; Hamilton, F. J.; Harwood, H. J. Silicon Chem 2002, 1, 107.
5. Yilgor, I.; Steckle, W. P.; Yilgor, E.; Freelin, R. G.; Riffle, J. S. J Polym Sci Part A: Polym Chem 1989, 27, 3673.
6. Yildiz, Y.; Uyanik, N.; Erbil, C. J Macromol Sci Part A: Pure Appl Chem 2006, 43, 1091.
7. Crivello, J. V.; Conlon, D. A.; Lee, J. L. J Polym Sci Part A: Polym Chem 1986, 24, 1197.