

# Synthesis and Evaluation of Isopropyl Alcohol-Miscible Copolymers as Sprayable Skin Protective Barriers

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**Statement of Purpose:** Protection of compromised tissues as in lacerated, abraded, or incised skin has been of interest to clinicians for decades. This began with what is now described as the “traditional bandage,” followed by the development of highly conformable, adhering, thin films of materials such as polyurethanes with acrylic adhesives. These films provide a barrier to external contamination while allowing both oxygen and water vapor transmission to enhance epidermal regeneration and reduce scab formation. Most notably are films containing 2-hydroxyethyl methacrylate<sup>1</sup> which can be problematic in areas of the body exposed to water. A siloxane-containing polymer and solvent system is claimed to provide films which act as conformable bandages adhering to and protecting skin from contamination and desiccation, while allowing body fluid evaporation.<sup>2</sup> However, these films exhibit low tear strength and do not adhere to moist tissue for sufficient periods. The concept of using segmented amphiphilic non-absorbable copolymer solutions in isopropyl alcohol (IPA) as sprayable film-forming precursors of protective skin barriers, which are not disadvantaged by the undesirable properties of earlier films, was disclosed recently.<sup>3</sup> This report addresses the synthesis of these segmented amphiphilic non-absorbable copolymers and their evaluation as skin protective barriers.

**Methods: Series I** copolymers were synthesized in two steps. The first step was based on an N-vinyl-2-pyrrolidone (NVP) rich comonomer mixture, wherein NVP, n-hexyl methacrylate (HMA), 1,4-dioxane and 2-2' Azobisisobutyronitrile were mixed/dissolved and stirred at 65°C for 30 minutes. In the second step, HMA, 1,4-dioxane, and 2-2' Azobisisobutyronitrile were mixed/dissolved and incrementally added to the product of the first step over 16 hours. **Series II** copolymers were synthesized in the same manner as series I with iso-butyl methacrylate (IBMA) being mixed and added in the second step charge. The resulting copolymers were purified by multiple precipitations and evaluated for composition by elemental nitrogen analysis and infrared and for molecular weight by GPC. Copolymer films having a thickness of 45-60µm were prepared by solution casting from IPA. Mechanical properties of films were measured using an 858 MiniBionix® Universal Tester (MTS Systems Corporation, Eden Prairie, MN), their water vapor transmission (WVTR) was measured using a Permatran-W600 (Mocon, Minneapolis, MN) at 37°C and 100% relative humidity, and then oxygen permeability (OP) was measured using a Mocon Oxtran 2/20(ST system) at 35°C and 0% relative humidity.

**Results / Discussion:** To obtain the desired mechanical and barrier properties, amphiphilic segmented copolymeric systems were structurally designed, prepared and converted to thin films. As noted in Table I, two series of copolymers were synthesized in order to study

incorporating hydrophobic vs. hydrophilic as well as high Tg vs. low Tg components in the copolymer chains. For series I, NVP segments were incorporated as the hydrophilic and high Tg component, and HMA segments were incorporated as the hydrophobic and low Tg component. In order to modulate the barrier properties without compromising the mechanical properties, IBMA segments were incorporated series II copolymers as a hydrophobic component with a high Tg relative to that of the HMA. The HMA/IBMA molar ratio was fixed at 80/20 for series II. The verification of the viability of the design is reflected in physical properties data (Table II).

Table I. Composition and Analytical Data of Copolymers

Copolymer	HMA/IBMA/NVP (mol%)	Mn (kDa)	Mw (kDa)	Final %NVP (mole %)*
I-A	75/0/25	54.6	99.1	18.4
I-B	70/0/30	48.0	111.4	24.8
I-C	65/0/35	41.7	101.1	25.8
II-A	76/19/5	52.6	89.9	4.9
II-B	72/18/10	51.6	93.3	9.9
II-C	64/16/20	51.8	99.9	18.2
II-D	56/14/30	47.0	103.4	21.9
II-E	48/12/40	42.8	106.9	32.9

\*assuming 80/20 HMA/IBMA molar ratio

Table II. Mechanical Properties of Films

Copolymer Film	Peak Stress (MPa)	Modulus (MPa)	Elongation (%)
I-A	3.8	17.2	440.9
I-B	3.3	39.8	228.1
I-C	3.5	37.4	190.4
II-A	1.8	9.4	637.3
II-B	2.5	15.6	312.3
II-C	7.3	91.9	303.9
II-D	6.2	115.9	249.4
II-E	6.8	150.2	188.7

Series I and II films exhibited an average WVTR of 130 and 19 (g/m<sup>2</sup>d)µm respectively with no significant differences within series. The addition of IBMA segments decreased WVTR due to the hydrophobic, fixed (high Tg) nature of these segments. The OP for series II films ranged from 14,000 to 40,000 (cc/m<sup>2</sup>d)100 µm and was inversely proportional to the high Tg/low Tg segment ratio due to the dynamic environment characteristic of low Tg segments.

**Conclusions:** Two series of IPA-miscible, segmented amphiphilic copolymers were synthesized and converted to thin films with modulated mechanical and barrier properties. Available properties of resulting films reflect their potential use as sprayable skin protective barriers or surgical drapes.

## References:

1. D'Andrea, M.J. U.S. Patent No. 4,303,066.
2. Salamone et al. U.S. Patent No. 4,987,893.
3. Shalaby, S.W. et al., U.S. Patent appl. 2004.