Acrylic Block Copolymer for Adhesive Application

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Introduction

Kuraray Co., Ltd. has recently developed a number of completely acrylic block copolymers through the use of its novel polymerization technologies [1][2]. The structures of the copolymers are tri-block copolymers, i.e. poly(methyl methacrylate)-block-poly(n-butyl acrylate)-block-poly(methyl methacrylate) (M-nBA-M) (Figure 1). These acrylic block copolymers can be used in high performance Pressure Sensitive Adhesives (PSA) applications demanding optical clarity, versatility of adhesion, weatherability, durability and low viscosity. The low viscosity and tri-block structure enable one to make high solid content, solvent based adhesives or use them in 100 % solids hot melt systems without a chemical crosslink. More recently, we have developed a new family of acrylic block copolymers using 2-ethyl hexyl acrylate (EHA) monomer. When compared with nBA, EHA-type acrylic block copolymers have several strong points, including low temperature properties, tackiness, high cohesion, and miscibility with tackifiers. In this paper, the characteristics and possible adhesive applications of nBA-type and EHA-type acrylic block copolymers are shown.

Synthesis and Structure

Figure 1 shows the molecular structure of the acrylic block copolymer, which is a completely (meth)acrylic triblock polymer. It is sequentially synthesized using our living anionic polymerization at moderate temperatures. These block polymers are built of two terminal hard PMMA blocks (Tg = 100 ~ 120 °C) and one inner soft rubbery poly(n-butyl acrylate) (PnBA) midblock (Tg = –40 ~ –50 °C). These block copolymers have a very narrow molecular weight distribution (Mw/Mn = 1.1 ~ 1.3). A well-defined diblock polymer can be synthesized using similar techniques.

As determined by SEC (size exclusion chromatography), the molecular weight distributions of the acrylic block copolymer and conventionally made PnBA can be seen in Figure 2. The molecular weight distribution of the acrylic block copolymer is much narrower than that of a conventional acrylic polymer. Moreover, the acrylic block copolymer has a well-defined structure and a very low residual content of monomers and oligomers.

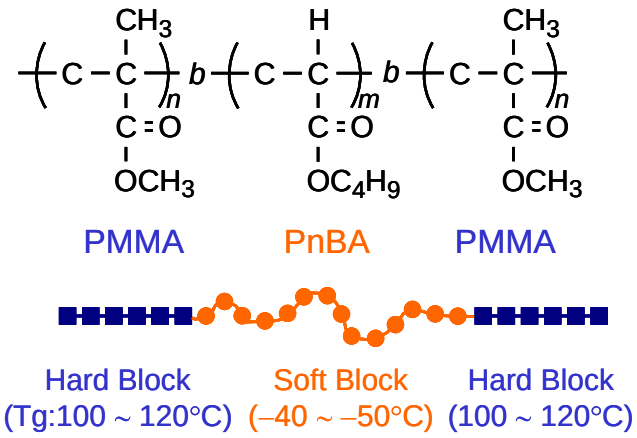

Figure 1. Structure of the acrylic block copolymer produced through living anionic sequential polymerization.

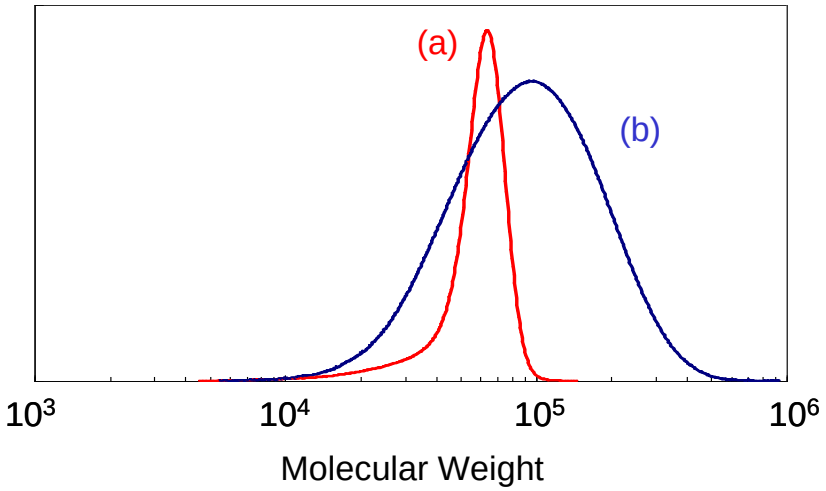

Figure 2. SEC(Size Extrusion Chromatography) and molecular weight distribution curves of (a) acrylic block copolymer by our living anionic system(Mw/Mn=1.13), and (b) conventionally made PnBA(Mw/Mn=1.56).

Morphology

Through the use of a specified staining method, the morphology of acrylic block copolymers using Transmission Electron Microscopy (TEM) is possible (Figure 3). The TEM photo shows that the acrylic block copolymer has a well-defined structure. The micro phase separation is very clear and the sample shows cylindrically arranged dark PMMA micro domains with an approximate diameter size of ca. 20 nm in a light PnBA matrix. The acrylic block copolymers have different micro phase domain morphologies, which depend on the content ratio of PMMA block to PnBA block:

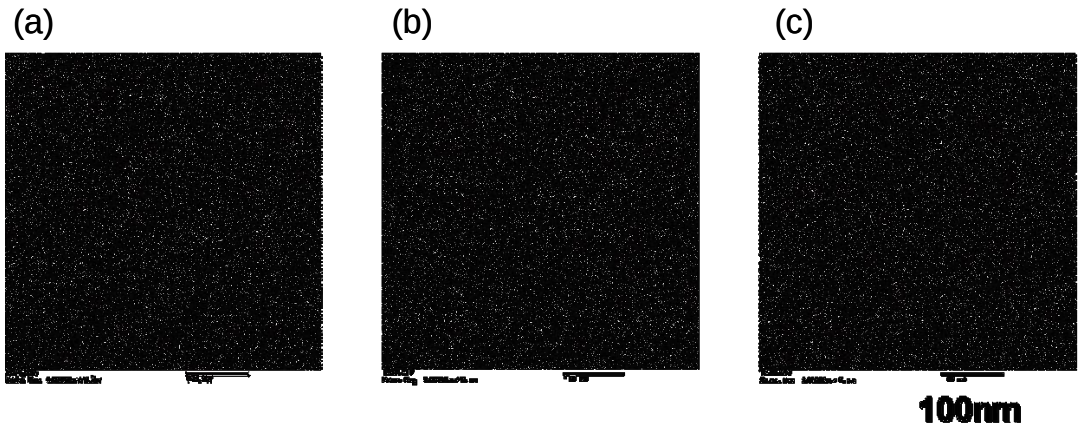

Figure 3. Morphology of acrylic block copolymers by TEM. (a) Short cylindrical morphology for M-nBA-M 1 (low PMMA content), (b) Long cylindrical morphology for M-nBA-M 2 (mid PMMA content.), and (c) Lamellar morphology for M-nBA-M 3 (high PMMA content).

Rheology

Dynamic mechanical analysis (DMA) of the acrylic block copolymers indicate the elastic modulus of the different molecular structures (Figure 4). These materials can be used in a variety of applications including injection molded materials, films, resin modifiers and pressure sensitive adhesives, i.e. PSA. The elastic modulus range is very suitable for PSA applications since tackifiers and plasticizers are not essential for PSA formulations.

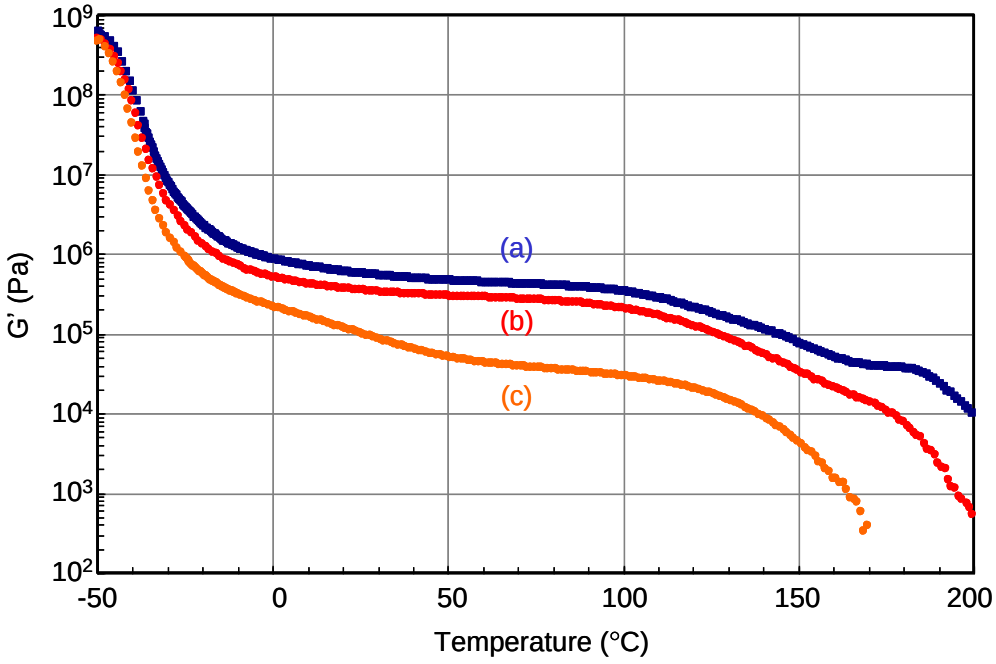

Figure 4. DMA curves of acrylic block copolymers. (a) M-nBA-M 2 (mid PMMA content), (b) M-nBA-M 1 (low PMMA content), and (c) M-nBA-M 1 / M-nBA = 50wt%/50wt%. M-nBA is the very low PMMA content diblock polymer which is in liquid form.

Miscibility of Acrylic Block Copolymers and Tackifiers

In designing a PSA formulation with acrylic block copolymers, the miscibility with tackifiers needs to be considered. In principle, tackifiers and plasticizers should be selectively compatible with the PnBA block domain. Miscibility data of acrylic block copolymer/tackifier systems are shown in Figure 5 via tan delta curves. With increasing tackifier content, the glass transistion temperature, Tg, of the PnBA block shifts to a higher temperature. This indicates that the PnBA block and tackifier are miscible. In high tackifier content formulations, it is noted that the PnBA domain becomes saturated and the tackifier becomes free. (Figure 5(c))

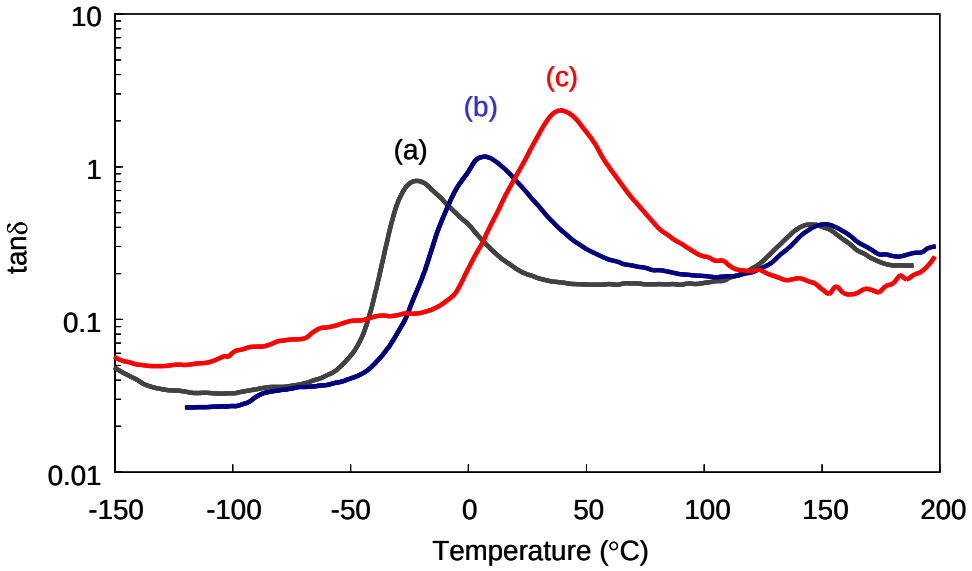

Figure 5. Effect of tackifier content on the loss tangent (tan δ) of acrylic block polymer / tackifier systems. M-nBA-M 1 / tackifier = (a)100/0, (b)100/30, and (c)100/100. Tackifier is a hydrogenated rosin ester type.

Block Copolymers Using Long-Chain Alkyl Acrylate as the Soft Block

EHA is a popular monomer in conventional crosslinked acrylic PSAs. Similarly, to nBA, EHA can be utilized in the living anionic polymerization system. DMA curve of M-EHA-M indicates micro phase separation is sharp as well as M-nBA-M (Figure 6).

Figure 6 also indicates the Tg shifts to lower temperatures with an increase in EHA ratio of the soft block. This should give rise to an improvement of low temperature properties. And, the cohesion of EHA type is superior to that of the nBA-type. This is confirmed by a creep test and SAFT (shear adhesion failure temperature) test. Additional benefits of EHA-type block copolymers were confirmed including improved tackiness and miscibility with tackifiers.

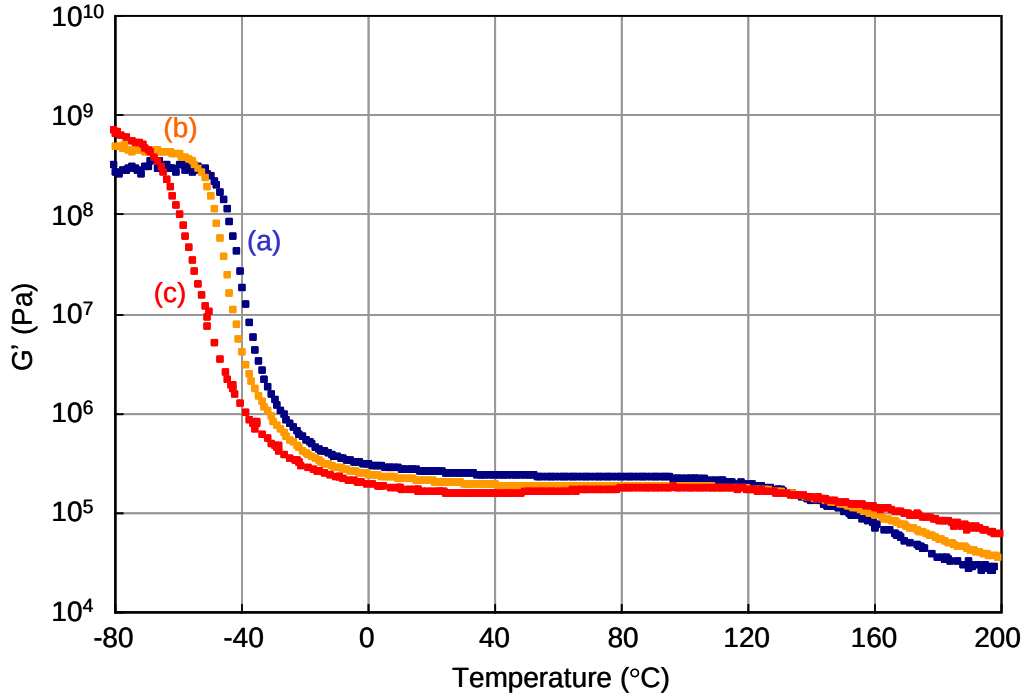

Figure 6. DMA curves of three types of acrylic block copolymers with equivalent molecular weight. The soft block consists of (a) nBA/EHA = 100/0, (b) nBA/EHA = 80/20, and (c) nBA/EHA = 0/100.

Adhesives Properties

PSA properties can be controlled by altering the PMMA contents of the block copolymer and/or by the formulation of triblock and diblock. In this case, the range of peel strength is 0.1-10 N/25mm (to steel). By formulating with diblock, the initial adhesive strength increases and its change with time decreases. Formulations with tackifiers have higher adhesive strengths, which range from 10-20 N/25mm (to steel) (Figure 7). The PSA performance of the formulated adhesives is shown in Table 1. It is clear that the acrylic block copolymer formulations have excellent cohesion and lower viscosities than other conventional materials (hot melt rubber adhesives and crosslinked acrylic PSA).

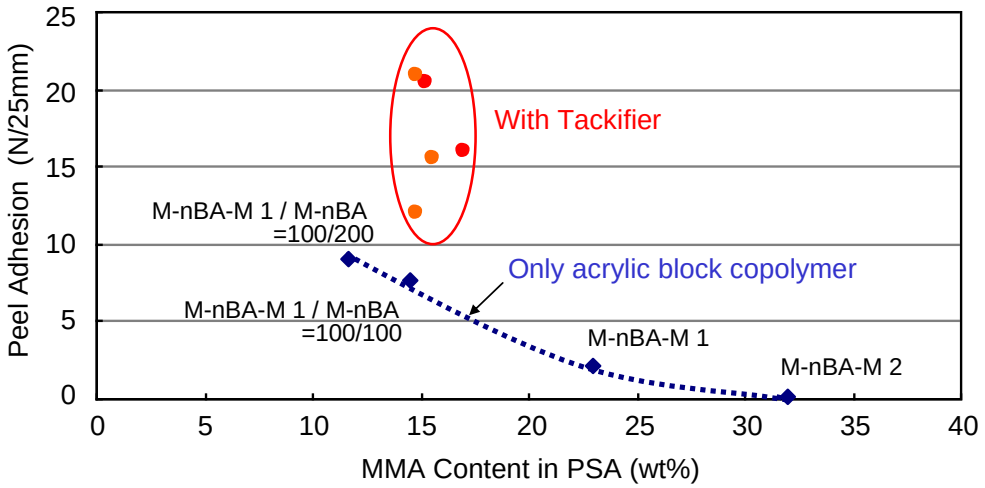

Figure 7. Adhesion strength of acrylic block copolymer and tackifier formulations. (thickness =25μm, 180° peel strength, peel speed =300mm/min)

Table 1. PSA Formulations and Properties

	1	**2**	**3**	**4**	**CE1**	**CE2**
Formulation						
M-nBA-M (low PMMA cont.)	100	100	100	100		
M-nBA (low PMMA cont. in liquid form)	0	20	0	0	Hot Melt Rubber Adhesive	Double sided acrylic tape with non-woven fabric base film
Tackifier A (Rosin Ester)	35	35	35	0		
Tackifier B (Aromatic Resin)	0	0	0	35		
Plasticizer (Acrylic oligomer)	0	0	20	20		
Coating Thickness (μm)	53	58	64	62	35	165
Rolling Ball Tack Test *	7	8	11	7	<4	16
Creep Test (Holding power at 80°C)	> 1week	> 1week	> 1week	26hr	10min	9.6hr
180° Peel Adhesion						
to Stainless Steel (N/25mm)	16	15	12	21	27	32
to PE (N/25mm)	8.6	6.9	7.6	7.8	20	14
Viscosity at 180°C (mPa/s)	30,000	24,000	10,000	16,000	51,000	n.d.

Test Piece: PET(50μm)/PSA (casted by Toluene solution)
Test Condition: * JIS test method (The larger ball number means better tack),
Creep test: Load lkg, Sample size 25mm×25mm,
180° Peel Test: 300mm/min at r.t.,
Viscosity: measured by "Brookfield viscometer"

Conclusions

A novel all (meth)acrylic block copolymer has been developed. Properties of M-nBA-M and M-EHA-M produced with novel anionic living polymerization were shown. The thermoplastic behavior and low viscosity of these polymers provide benefits in hot melt PSA. On the other hand, the Tg of PMMA block is high enough for normal applications. These materials are also well suited for solution coat PSA. Advantages of these materials are summarized in table 2. Formulating with these acrylic block copolymers can give rise to high performance PSA.

Table 2. Characteristics of Acrylic Block Copolymers by Anionic Living Polymerization

Characteristics	Advantages
All acrylic structure	✓ Good transparency
	✓ Weatherability
	✓ Moisture permeability
Narrow molecular weight distribution	✓ Non-staining
	✓ No odor
Physical crosslink	✓ High productivity
	✓ High cohesion below the Tg of PMMA
	✓ Recyclable
Non aging process	✓ High productivity
	✓ Stable adhesion properties,
No crosslink agents	✓ Stable adhesion properties
No acrylic acid	✓ Nonstaining
Low viscosity	✓ Hot melt productivity
	✓ High solid content in solution

References

1) United States Patent 6,329,480
2) United States Patent 6,555,637